EMISSION MEASUREMENTS AND MODELLING SESSIONS

PHEM AND NEMO: TOOLS FOR MICRO AND MESO-SCALE EMISSION MODELLING

M. Rexeis, S. Hausberger, M. Zallinger, C. Kurz - Institute for Internal Combustion Engines and Thermodynamics, Graz University of Technology, Inffeldgasse 21a, A- 8010 Graz Austria

FACTORS INFLUENCING PM_{10} EMISSIONS FROM ROAD PAVEMENT WEAR

M. Gustafsson[1], G. Blomqvist[1] A. Gudmundsson[2], A. Dahl[2], P. Jonsson[1] & E. Swietlicki[2] - [1]Swedish National Road and Transport Research Institute (VTI), Linköping, Sweden, [2]Lund University of Technology, Lund, Sweden

REAL-WORLD NO AND NO_2 EMISSION FACTORS OF MODERN LIGHT VEHICLES, DERIVED FROM RELIABLE ONLINE MEASUREMENTS

Robert Alvarez[1], Martin Weilenmann[1], Jean-Yves Favez[1] - [1]Empa, Swiss Federal Laboratories for Materials Testing and Research, Laboratory for Corrosion and Materials Integrity; Ueberlandstrasse 129, CH-8600 Duebendorf, Switzerland.

COLD START EMISSIONS OF PASSENGER CARS AT DIFFERENT LOW AMBIENT TEMPERATURES

Jean-Yves Favez[1] and Martin Weilenmann[1] - [1]Empa, Swiss Federal Laboratories for Materials Testing and Research, Laboratory for Internal Combustion Engines; Ueberlandstrasse 129, CH-8600 Duebendorf, Switzerland.

THE MOBILE LABORATORY "SNIFFER" FOR NON-EXHAUST EMISSION MEASUREMENTS: VALIDATION OF THE SYSTEM AND THE FIRST RESULTS

Pirjola, L.[1,2], Kupiainen, K.[3,4] and Tervahattu, H.[3] - [1]Helsinki Polytechnic, Department of Technology, P.O. Box 4020, FIN-00099 Helsinki, Finland, [2]University of Helsinki, Department of Physical Sciences, P.O. Box 64, FIN-00014 Helsinki, Finland, [3]Nordic Envicon Oy, Koetilantie 3, FIN-00790 Helsinki, Finland, [4]University of Helsinki, Department of Biological and Environmental Sciences, P.O. Box 56, FIN-00014 University of Helsinki

EVALUATING AN URBAN EMISSIONS INVENTORY MODEL USING MULTI-REGRESSION AIR POLLUTION MAPS FROM EXTENSIVE MONITORING

S. Mesquita[1] , F. Ferreira[1], V. Gois[2], P. Torres[1], L. Nogueira[3], J. Monjardino[1], C. Almeida[3], H. Maciel[2] - 1 Departamento de Ciências e Engenharia do Ambiente, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, Quinta da Torre, 2829-516 Caparica, Portugal, 2 InventAr, R. Sarmento Beires 15-8E, 1900-410, Lisboa, Portugal, 3 Comissão de Coordenação e Desenvolvimento Regional de Lisboa e Vale do Tejo, Rua Bramcamp, 7, 1250-048 Lisboa, Portugal

THE INFLUENCE OF GEAR CHANGE ON VEHICLE EXHAUST EMISSIONS. CALCULATIONS WITH THE VETESS EMISSION TOOL

[1,2]Beckx, C., [1]Int Panis, L., [2]Janssens, D., [1]De Vlieger, I.. and [2]Wets, G. - [1]Flemish Institute of Technological Research, Boeretang 200, 2400 Mol – Belgium, [2]Transportation Research Institute - Hasselt University, Wetenschapspark 5/6, 3590 Diepenbeek - Belgium

HEAVY METALS EMISSION INVENTORY IN THE CZECH REPUBLIC

Jitka Hlavicova[1], Ilona Dvorakova[1], Radomir Srnensky[2] - [1]Czech Hydrometeorological Institute, Prague, [2]IDEA –ENVI s.r.o., Valasske Mezirici

EMISSION INVENTORY OF CARBON MONOXIDE AND NITROGEN OXIDES FOR AREA SOURCES AT BUENOS AIRES METROPOLITAN AREA (ARGENTINA)

A. L. Pineda Rojas, L. E. Venegas and N. A. Mazzeo - National Scientific and Technological Research Council (CONICET), Department of Atmospheric and Oceanic Sciences, Faculty of Sciences. University of Buenos Aires, Ciudad Universitaria. Pab. 2. 1428-Buenos Aires. Argentina.

COMPILATION OF AIR EMISSION INVENTORIES FOR WESTERN MACEDONIA, GREECE

D. Vlachogiannis[1], A. Sfetsos[1,2], N. Gounaris[1], J.G. Bartzis[2] - [1] Environmental Research Laboratory, INT-RP, NCSR Demokritos, Patriarchou Grigoriou & Neapoleos Str.,15310, Aghia Paraskevi, Greece, [2]University of Western Macedonia,Dept. of Energy Resources Engineering, Salvera & Bakola Str., 50100, Kozani, Greece

CARBON AND OXYGEN ISOTOPE COMPOSITION OF ANTHROPOGENIC CO_2 SOURCES IN THE URBAN ENVIRONMENT

M. Zimnoch, M. Mlicki, K. Rozanski - Faculty of Physics and Applied Computer Science, AGH University of Science and Technology, Al. Mickiewicza 30, 30-059 Krakow, Poland

PHEM AND NEMO: TOOLS FOR MICRO AND MESO-SCALE EMISSION MODELLING

M. Rexeis, S. Hausberger, M. Zallinger, C. Kurz
Institute for Internal Combustion Engines and Thermodynamics, Graz University of Technology,
Inffeldgasse 21a, A- 8010 Graz Austria (rexeis@vkmb.tugraz.at)

ABSTRACT
From the huge data pool of ARTEMIS, COST 346 and HBEFA, two new traffic emission models have been elaborated at the University of Technology in Graz, which are to be used to fill existing gaps in integrated air quality modelling. These models are the micro-scale model "PHEM" and the meso-scale model "NEMO".

1. INTRODUCTION

Emission models have to be based on emission measurements on a representative number of engines and vehicles from all relevant vehicle categories, propulsion systems and steps of exhaust gas legislation. In total, tests on hundreds of vehicles are necessary to gain representative emission values for vehicle fleets. This makes the data base for reliable models very expensive and difficult to handle. For this reason, several international co-operations and projects were launched during past years to pool existing data from national projects, to elaborate new data sets on modern vehicles and to develop modern data base and simulation tools for vehicle emission models (e.g. ARTEMIS, COST 346, HBEFA).
From the huge data pool of these projects, two new emission models have been elaborated at the University of Technology in Graz, which are to be used to fill existing gaps in integrated air quality modelling. These models are:

- PHEM (Passenger car and Heavy duty vehicle Emission Model), a micro-scale model for the simulation of the exhaust gas emissions of single vehicles in 1Hz resolution.
- NEMO (Network Emission Model), a meso-scale model for the simulation of emissions on road networks with integrated calculation of fleet composition and emission simulation on a vehicle level.

Both models make use of the same huge data base on measured vehicles and engines for the simulation of fleet emissions and are compatible with the HBEFA 2.1 to a large extent. Additionally, a set of emission tests on vehicles with years of production of 2003 and newer have been implemented in PHEM and NEMO.

2. PHEM – PASSENGER CAR AND HEAVY DUTY EMISSION MODEL

The instantaneous emission model PHEM (Passenger car and Heavy duty Emission Model) is designed for simulating emissions and fuel consumption of single vehicles in 1 Hz resolution on a very detailed modelling scale. It has been in the process of development at the Institute for Internal Combustion Engines and Thermodynamics since 1999 in the course of the projects ARTEMIS and HBEFA.

Model Structure

With a given driving cycle and road gradient, the effective engine power is calculated in 1Hz frequency from the driving resistances and losses in the transmission system. The actual engine speed is simulated by the transmission ratios and the gear shift model of an average driver. The emissions are then interpolated from engine maps.
For the detailed emission simulation, several data sets on vehicle specifications and operation patterns are necessary, which are saved in the vehicle data file, the full load curve, the engine map, the driving cycle, dynamic correction functions and several files with cold start conditions. A detailed description of the model is given in (Zallinger et al., 2005).
A method to obtain engine emission maps from transient vehicle tests on the roller test bed was elaborated to integrate a broader data set into the model. At the beginning of 2007, the model data base consists of 102 heavy duty engines and 32 passenger cars.
Basically, PHEM is capable of simulating the fuel consumption and the emissions for any driving cycle with any vehicle configuration. Additionally, the emission simulation is much closer to the relevant parameters of the combustion and to the parameters used for the application of the engine control unit. As a result, it was possible to develop functions (dynamic corrections) which were able to take the influence of different transient conditions in driving cycles on the emission levels into consideration. This "transient correction" is derived from empirical functions which transform the emission levels of each single point in the engine map into the emission levels that are to be expected under the actual transient engine load in the simulated cycle.

By this methodology, PHEM is capable of simulating single specific vehicles as well as the "average" emission behaviour of, for example, diesel or gasoline cars from EURO 0 to EURO 4. Appropriate to the fields of application, PHEM has an interface with the microscale traffic simulation tool VISSIM or similar models.
The emission model PHEM has been validated very successfully in several projects and publications. This has primarily been done by a comparison of model results with measured emissions in driving cycles, which have not been used for the model setup. A validation of PHEM for the simulation of emissions of passenger cars based on chassis dynamometer tests can be found, for example, in (Zallinger, 2005), and a model validation is given for heavy duty vehicles, for example, in (Hausberger, 2002) based on a chassis dynamometer test and in (Soltic, 2004) based on on-board measurements.

Example of Model Application and Results

For a detailed ascertainment of the emissions of the road traffic in the city of Graz in Austria, a survey of the driving behaviour of passenger cars and consecutive simulations by the model PHEM have been performed (Schodl, 2005). In a first step, the street network of Graz was classified into a set of seven different street categories. For each category, the typical driving behaviour of passenger cars was measured by test drives with a car equipped with a GPS system. Additionally, the temporal traffic density during the test drives was recorded, based on automatic traffic counts. For each combination of street category and traffic density, the recorded driving patterns were then used as input for the emission model PHEM for the simulation of the corresponding traffic emission levels.
Figure 1 gives an example of the results for NO_x emissions of EURO 3 diesel passenger cars on two types of urban main streets with a speed limit of 50 km/h, and a comparison with the emission factors for the corresponding traffic situations from the "Handbook emission factors for road transport" (HBEFA 2.1). Despite the similar speed limits on both street categories, the results clearly show a higher emission level for the street category "city centre", which can be mainly attributed to the shorter distances between the intersections in the inner urban case. For stop and go traffic, no significant difference in the driving behaviour between the different street categories was found. Therefore, the same cycle was applied for the simulation of emissions for all street categories for this traffic situation (defined by the occurrence of vehicle stops even when not at intersection areas). Compared to the emission level for lower traffic densities, stop and go conditions for district distributor roads were found to approximately double the NO_x emission levels.

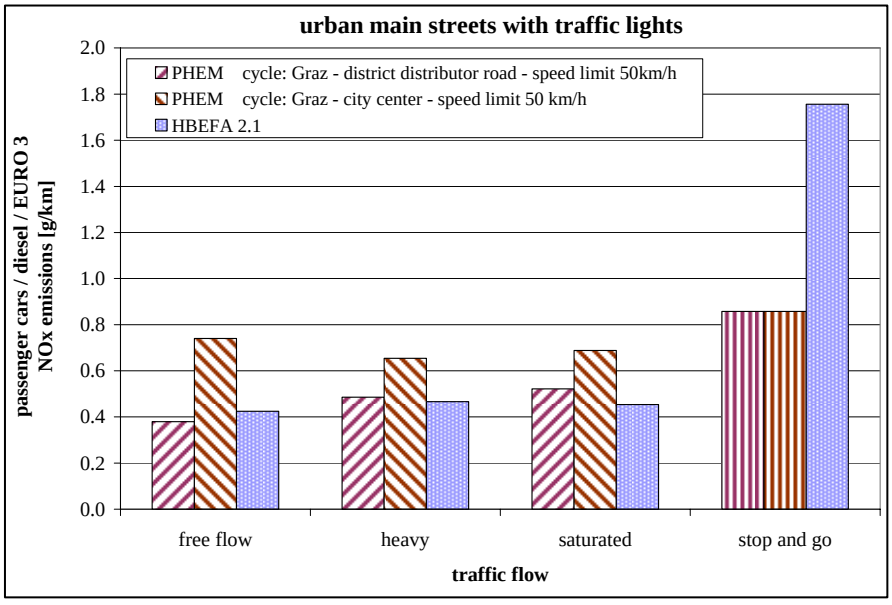


Figure 1: Comparison emission factors for urban main streets at different traffic densities

The ascertainment of the NO_x emissions of EURO 3 passenger cars based on the HBEFA 2.1 gives comparable results for traffic densities up to "saturated" conditions for district distributor roads, but an underestimation up to 40% for main roads in the city centre. Conversely, the HBEFA 2.1 predicts approximately twice the NO_x emission level found in the simulations for the Graz case for stop and go traffic. The average vehicle speed of the underlying driving cycles is also different: Whereas in the HBEFA 2.1 an average speed of 5 km/h is used for the specification of the urban stop and go emissions, an average vehicle speed of 10 km/h was found to be the "average" for stop and go conditions in Graz.
The results show that the HBEFA2.1 cannot be representative for all local traffic situations. Thus, an accurate simulation of traffic emissions on a spatial high resolution level or the evaluation of complex measures in road transport (like the implementation of speed limits, or the replacement of intersections by roundabouts) requires a

combination of detailed analysis of the driving behaviour and a micro-scale emission model, which is able to predict vehicle emission for any kind of driving cycle.

3. NEMO – NETWORK EMISSION MODEL

The model "NEMO" (Network Emission Model) is being specially developed for an accurate and efficient calculation of vehicle emissions in road networks.

Model Structure

For the overall emission output on road networks, the proportions of the different vehicle layers on the overall mileage are relevant. In contrast to PHEM, NEMO also includes a detailed simulation of the fleet composition. In NEMO, the fleet is divided into what are known as "vehicle layers" that have homogenous emission behaviour. A vehicle layer is, for example, a "rigid truck with diesel engine, maximum allowed gross vehicle weight between 7.5 and 15 tons, first registered under the emission legislation EURO III, no additional exhaust gas aftertreatment". The calculation of the proportions of the different vehicle layers on the overall traffic volume is done as a function of the year considered and the road type.

Like in PHEM, the emission simulation is also calculated for a single vehicle level, but the calculation of the required engine power is based on average values (velocities, cinematic parameters for the description of the cycle dynamics) for the local driving behaviour under consideration. The reason for this can be found in the fact that no 1Hz data for the driving behaviour of all vehicles under consideration is generally available for the traffic flow on road networks. An additional benefit of the calculation based on average cinematic parameters, but not on 1 Hz data is the much quicker computing time. Based on the required engine power, the emissions are then interpolated from engine polygons. This is done for each road section in the simulated network.

With its flexible model structure, NEMO is completely applicable for the evaluation of different case scenarios. The features implemented into the model enable, for example, the illustration of the effects of varying the driving behaviour (e.g. traffic calming) or of special actions that have an effect on the fleet composition (e.g. promotion programs for diesel vehicles with exhaust aftertreatment or retrofit programs) on the fleet emissions. Appropriate to the fields of application, NEMO has a link to meso-scale traffic simulation models like VISUM. The results from NEMO can be imported into the air quality model GRAL (Öttl, 2002), (Öttl, 2003) to complete the integrated air quality modelling approach.

The model validation of NEMO has been performed by comparing model results for all vehicle categories in a widespread set of driving conditions with the emission model PHEM and the HBEFA 2.1. More details on NEMO can be found in (Rexeis, 2005).

Example of Model Application and Results

The model NEMO has been applied for the evaluation of the effects of the introduction of a "city toll" for the extended city centre of Graz on the local air quality. For the year 2010, the emissions and the air quality have been simulated by the linked models NEMO and GRAL for both a "business as usual" scenario and a "city toll" scenario. For the latter case, a fee of €2 for passenger cars entering the charging zone was assumed. The effects on the traffic volume have been taken from literature and transferred to a street network level into the emission model. Inside the charging zone, a clear decrease of the mileage of passenger cars was assessed, whereas an increase of the traffic volume is expected at the outer ring of the zone. In general, a shift of passenger kilometres from individual traffic to public transport is predicted. In total, a decrease of 5% in vehicle kilometres is expected for the entire city area of Graz. For PM10, the emissions from the transport sector decrease slightly (approx. -1%), and a small increase is predicted for the emissions of NOx (approx. +1 mainly because of the rise in bus kilometres in public transport). On the small scale local level, both slight improvements and small declines of the air quality can be expected. For PM_{10} the modelled effects of the introduction of a city toll on the yearly average concentrations are in a range of ±1,5 µg/m³ (Figure 2).

The effects of more than 20 other road traffic related measures on the emissions and air quality for several regions within Austria have been investigated by NEMO and PHEM so far. The analysed strategies include, for example, measures influencing the driving behaviour (e.g. traffic calming), and special actions having an effect on the fleet composition (e.g. retrofit promotion programs for diesel vehicles with exhaust aftertreatment).

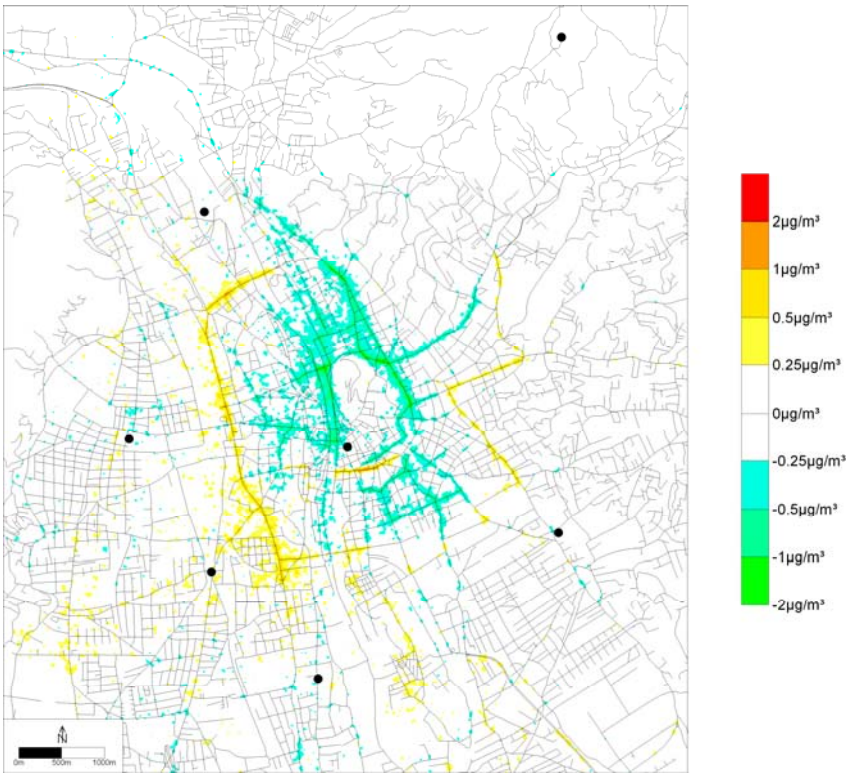


Figure 2: Simulated effects of the introduction of a city toll for the extended city centre of Graz on the yearly average PM10 concentration in the year 2010. *(yearly average PM10 concentrations in the area under investigation are 32 to 47 µg/m³)*

4. SUMMARY

Emission factors from global models like HBEFA or CORINAIR cannot be representative for all local traffic conditions. Therefore, the micro-scale emission model PHEM has been developed at TU Graz. PHEM makes it possible to produce local emission factors as well as to analyse the local situation in detail. The disadvantage is the need for 1 Hz driving patterns as model input, which either can be measured on the road or simulated by micro-scale traffic models. On the meso-scale level, the model NEMO has been developed at TU Graz for the simulation of emissions on road networks. NEMO combines the calculation of the vehicle fleet composition and emission simulation. Appropriate to the fields of application, PHEM has an interface with the micro-scale traffic simulation tool VISSIM, while NEMO has a link to meso-scale traffic models like VISUM. The results from NEMO can be imported into the air quality model GRAL to complete the integrated air quality modelling approach.

5. ACKNOWLEDGEMENTS

We want to acknowledge all the partners from ARTEMIS, COST 346, HBEFA and the Austrian IG-Luft study for their inputs to the data base for the development of the models and the methods.

6. REFERENCES

Hausberger S. et al.: Update of the Emission Functions for Heavy Duty Vehicles in the Handbook Emission Factors for Road Traffic; Institute for Internal Combustion Engines and Thermodynamics; Graz 2002

Handbook Emission Factors for Road Transport (HBEFA) Version 2.1 (28. Feb. 2004); http://www.hbefa.net/

Öttl D., Almbauer R., Sturm P. J. (2001): A new method to estimate diffusion in low wind, stable conditions. Journal of Applied Meteorology, 40, 259-268.

Öttl, D., P. J. Sturm, M. Bacher, G. Pretterhofer, R. A. Almbauer (2002): A simple model for the dispersion of pollutants from a road tunnel portal. Atmos. Environ., 36, 2943-2953.

Rexeis M., Hausberger S.: Calculation of Vehicle Emissions in Road Networks with the model “NEMO”; Transport&Airpollution Conference; ISBN: 3-902465-16-6, Graz 2005

Schodl B. 2005. Fahrverhaltensuntersuchung zur Emissionssimulation. Diploma Thesis, Institute for Internal Combustion Engines, University of Technology Graz

Soltic P., Hausberger S.: On-Road Emission Measurements and Emission Modelling Results for a Tractor-Semitrailer in Trans-Alpine Operation; 13th International Scientific Symposium Transport and Air Pollution; Boulder, Colorado USA; September 13-15, 2004

Zallinger M., Le Anh T., Hausberger S. 2005. Improving an instantaneous emission model for passenger cars. Transport&Airpollution Conference Graz. ISBN: 3-902465-16-6

Proceedings of the 6th International Conference on Urban Air Quality
Limassol, Cyprus, 27-29 March 2007

FACTORS INFLUENCING PM_{10} EMISSIONS FROM ROAD PAVEMENT WEAR

M. Gustafsson[1], G. Blomqvist[1] A. Gudmundsson[2], A. Dahl[2], P. Jonsson[1] & E. Swietlicki[2]

[1]Swedish National Road and Transport Research Institute (VTI), Linköping, Sweden
[2]Lund University of Technology, Lund, Sweden

ABSTRACT

Accelerated pavement wear is one of the major environmental disadvantages of studded tyres in northern regions and results in increased levels of PM_{10}. Measurements of PM_{10} in a road simulator hall have been used to study the influence of pavement properties, tyre type and vehicle speed on pavement wear. The test set-up included three different pavements (one granite and two quartzite with different aggregate sizes), three different tyre types (studded, non-studded, summer tyres) and different speeds (30–70 km/h). The results show that the granite pavement was more prone to PM_{10} production compared to the quartzite pavements. Studded winter tyres yields tens of times higher PM_{10} concentrations compared to non-studded winter tyres. Wear from summer tyres was negligible in comparison. It was also shown that wear is strongly dependent on speed; every 10 km/h increase yielded an increase of the PM_{10} concentration of 680 µg m^{-3} in the simulator experiments.

1. INTRODUCTION

During the last years it has become evident that wear particles from road pavements and tyres strongly contribute to episodes with very high concentrations of inhalable particles in outdoor air. These episodes normally occur during dry periods in winter and spring when accelerated wear and particle production occurs due to the use of studded tyres and winter gritting. This problem has attracted attention especially in Norway (Hetland et al., 2000), Finland (Räisänen et al., 2003) and Sweden (Gustafsson et al., 2007). In some Norwegian cities the adverse health effects have led to the introduction of fees for motorists using studded tyres. Although pavements have been improved since the 1980's and studs nowadays mainly are made of lightweight alloys instead of steel, about 100 000 tons of pavement is worn each winter season in Sweden.

The resulting wear and production of inhalable particles is dependent on a number of factors that are difficult to quantify in real world environments. Therefore, the objective of this study was to investigate the effects of pavement type, tyre type and speed on pavement wear in a controlled environment. This was done by varying influencing factors individually (i.e. pavement type, tyre type, speed).

2. METHODOLOGY

At the Swedish National Road and Transport Research Institute (VTI) a circular road simulator was used to generate wear particles (Figure 1). Particle sampling in the simulator hall makes it possible to sample pure wear particles, with very low contamination from ambient particles. The road simulator runs four wheels around a circular track. Each wheel axle is equipped with an electrical motor which drives the rotation of the simulator. The speed can be varied between 0–70 km/h. An almost linear track simulation is accomplished even though the tyres are running in a circle since no radial force is acting on the tires as the wheels are bolted to the axles of the road simulator. To make the wheels move across the entire track, the vertical axle can be displaced by an eccentrical movement at speeds above 50 km/h.

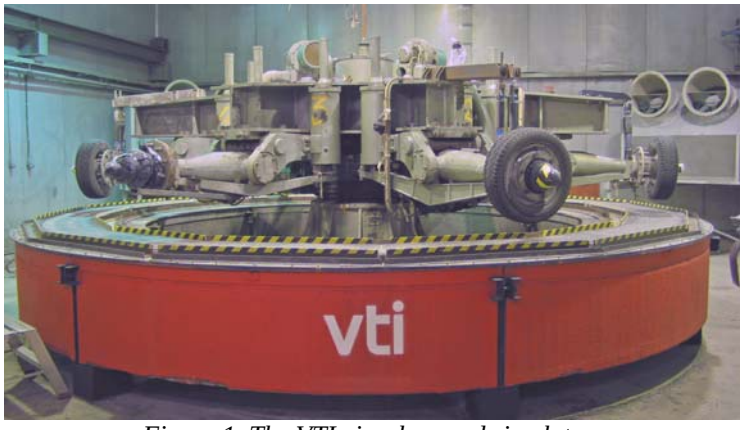


Figure 1. The VTI circular road simulator.

The simulator track can be equipped with any type of pavement and any type of light-duty vehicle tyre can be mounted on the axles. No ventilation of the simulator hall was used, but pressure gradients might have caused minor self ventilation. Temperature or humidity was not controlled. The air temperature was between 20 and 35°C.

2.1. Measurement scheme

Three different sets of measurements were made in order to elucidate the effect of three factors on pavement wear and generation of PM_{10}; these were 1) type of pavement, 2) type of tyres and 3) speed.

1) Regarding type of pavement, three varieties with different properties were used. These included an asphalt concrete consisting of granite stone material with 16 mm maximum aggregate size (hereafter denominated "Granite <16"), a stone mastic asphalt of quartzite stone material with 16 mm maximum aggregate size ("Quartzite <16") and another stone mastic asphalt ("Quartzite <11") of another quartzite stone material with 11 mm maximum aggregate size. This set-up enabled comparison of wear resistance between aggregate size and stone material. All pavements were tested in 70 km/h with studded tyres .

2) Differences in particle generation characteristics were also studied between different types of tyres. Three types that are frequent in Sweden were chosen; studded winter tyres, friction (non-studded winter) tyres and summer tyres from the same manufacturer. These tests were made at 30, 50 and 70 km/h.

3) Speed can be varied from 0–70 km/h in the road simulator. In the normal case, different pavements and tyres are studied with respect to pavement wear when speed is increased stepwise. The increase between these speeds is made quickly in less than two minutes. Once the desired speed has been reached the road simulator is left to run for ~1.5 h. An additional test was made where the speed was increased gradually in increments of 5 km/h, with an interval of 20 minutes.

2.2. Particle sampling

To be able to detect short time variations, mass concentration of PM_{10} was sampled with a DustTrak instrument (TSI) with an averaging time resolution of 3 seconds. The DustTrak was placed in the same position during all measurements, approximately 2 m from the edge of the road simulator and at a height above 0.5 m above the surface of the pavement.

3. RESULTS AND DISCUSSION

3.1. Influence of pavement type

Three commonly used pavements in Sweden (Granite <16, Quartzite <16 and Quartzite <11) were studied with respect to particle generation. Figure 2 shows the results of measurements made during one hour at 70 km/h with these different pavements. Two comparisons can be made. Firstly, the difference between quartzite and granite pavements with the same maximum aggregate size is obvious (upper and middle lines). The granite pavement produces PM_{10} concentrations that are almost 70 % higher in comparison to the quartzite pavement. The measured concentrations are, regardless of pavement, extreme as a result of the confined hall.

Secondly, the two pavements with similar (but originating from different quarries) stone material (quartzite), but with different maximum aggregate size (11 and 16 mm respectively), also exhibit large differences in resulting PM_{10} concentrations. The total wear of a pavement normally decreases with increasing aggregate size (Jacobson and Hornvall, 1999). However, it can be seen in this experiment that the properties of the different materials seem more important than aggregate size since the pavement with the smaller aggregate size (Quartzite <11) leads to less PM_{10} production than the coarser pavement (Quartzite <16).

These results indicate that by making proper choices regarding pavement material and maximum aggregate size, wear can be minimized. These results are in accordance with Räisänen et al. (2003) that describe

different materials' resistance to wear and states thatmafic, volcanic rock is the most resistant while granite is least resistant to wear.

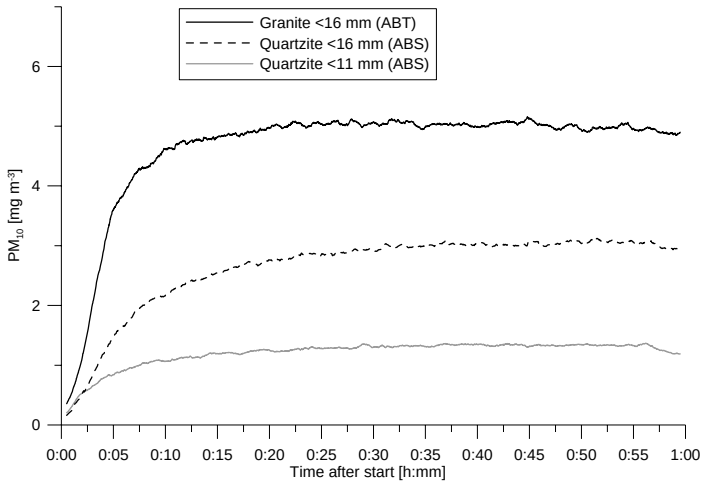


Figure 2. Measured concentrations of PM_{10} in the road simulator hall with different pavements (Granite <16 mm, Quartzite <16 mm and Quartzite <11 mm) under controlled ambient conditions. Road simulator speed was set to 70 km/h. Studded winter tyres were used.

3.1. Influence of tyre type

The severe particle production that studded tyres gives rise to compared to other tyres is obvious in Figure 3. The road simulator speed was 30, 50 and 70 km/h (at the time periods 11:30-13:00, 13:00-14:30 and 14:30-16:30, respectively). Studded tyres cause extreme concentrations of PM_{10} that are tens of times higher than those associated with non-studded winter tyres. These non-studded winter tyres are much less aggressive from a wear perspective. PM_{10} generated by summer tyres are almost negligible in this connection.

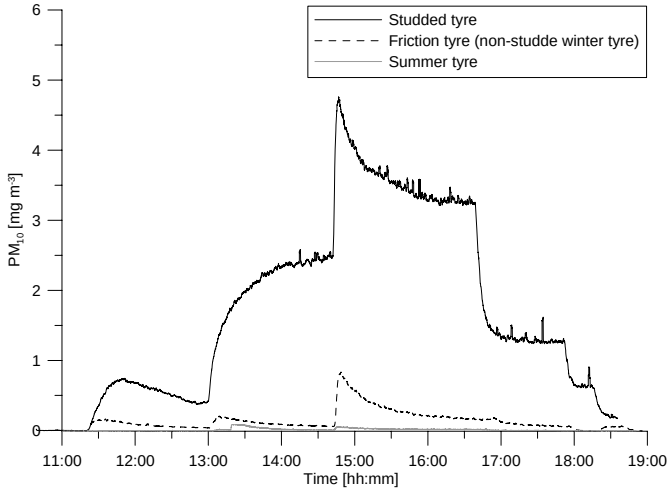


Figure 3. Measured concentrations of PM_{10} in the road simulator hall with different types of tyres (studded winter tyres, non-studded winter tyres and summer tyres). Road simulator speed was set to 30, 50 and 70 km/h, see description.

3.1. Speed dependency

In Figure 3 it can be seen that speed is a strong influencing factor on pavement wear. The maximum PM_{10} concentrations are reached at 70 km/h. However, when speed is increased momentarily in increments of 20 km/h some resuspension effects are included. This may conceal the real role speed has on pavement wear. In order to evade these effects the speed was instead increased gradually by increments of 5 km/h (Figure 4).

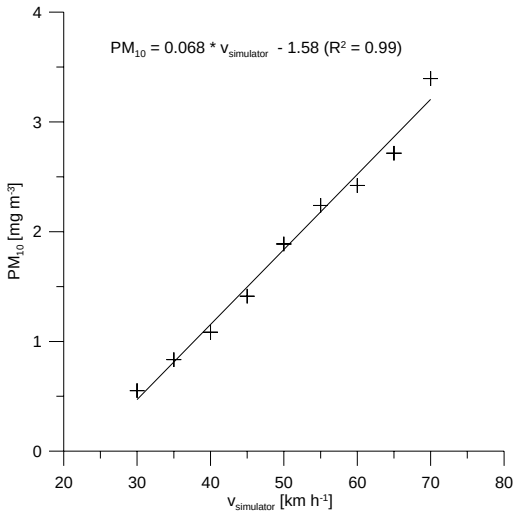


Figure 4. Measured concentrations of PM_{10} in the road simulator when speed is increased gradually (5 km/h increments with 10 minutes interval).

From these results it can be concluded that PM_{10} generation is highly dependent on vehicle speed. In Figure 3 one could suspect that pavement wear accelerates above a certain speed threshold, i.e. when speed is somewhere in the range between 30 and 70 km/h. However, Figure 4 shows that the measured concentration of PM_{10}, and probably therefore also pavement wear, increases linearly with speed (~680 µg m^{-3} for each 10 km/h increase). A complicating factor, not yet analysed, are the increased deposition velocity due to increased turbulence at higher PVM speed. Both these effects are likely to affect the linear relationship in figure 4. Whether these results can be translated to field environments awaits further research.

4. CONCLUSIONS

- A granite pavement resulted in 70 % higher PM_{10} concentration than a quartzite pavement of the same aggregate size. Out of two quartzite pavements with different aggregate sizes, the one with smaller stone material lead to lower PM_{10} concentration, indicating that other aggregate properties than size are more important for PM_{10} production.
- Studded winter tyres yields tens of times higher PM_{10} concentrations compared to non-studded winter tyres. Summer tyres have a very little effect on PM_{10} production in contrast.
- Speed is an equally important control over wear. At the measurement set-up used here, a 10 km/h increase in speed leads to a 680 µg m^{-3} increase of PM_{10} concentration in a linear fashion.

5. ACKNOWLEDGEMENTS

The Swedish National Road Administration is acknowledged for financial support.

6. REFERENCES

Gustafsson, M., Blomqvist G., Ljungman, A., Lindbom, J., Gudmundsson, A., Dahl, A. and Swietlicki, E. 2007. Characteristics and inflammatory potential of wear particles formed in a road simulator. UAQ 2007 Proceedings.

Hetland, R., Refsnes, M., Myran, T., Johansen, B., Uthus, N. and Schwarze, P. 2000. Mineral and/or metal content as critical determinants of particle-induced release of IL-6 and IL-8 from A549 cells. J Toxicol Environ Health A. Vol 60. No 1. pp 47-65.

Jacobson, T., Hornvall, F. 1999. Beläggningsslitage från dubbade fordon, VTI notat 44 (in Swedish). Swedish National Road and Transport Research Institute (VTI), lInköping, Sweden.

Räisänen, M., Kupiainen, K., Tervahattu, H. 2003. The effect of mineralogy, texture and mechanical properties of anti-skid and asphalt aggregates on urban dust. Bulletin of Engineering Geology and the Environment 62, 359-368.

REAL-WORLD NO AND NO_2 EMISSION FACTORS OF MODERN LIGHT VEHICLES, DERIVED FROM RELIABLE ONLINE MEASUREMENTS

Robert Alvarez[1], Martin Weilenmann[1], Jean-Yves Favez[1]
[1]Empa, Swiss Federal Laboratories for Materials Testing and Research, Laboratory for Corrosion and Materials Integrity; Ueberlandstrasse 129, CH-8600 Duebendorf, Switzerland.
Phone: +41 44 823 48 69, fax: +41 44 823 40 44, robert.alvarez@empa.ch

ABSTRACT
Nitrogen oxides (NO_x) are an inevitable combustion product originating from engines, furnaces and agricultural activities. Although NO_x levels have fallen sharply, roadside concentrations of nitrogen dioxide (NO_2) have stabilized. This observation leads to a need to obtain reliable emission factors for NO and NO_2 of road vehicles, while only NO_x is recorded in standard measurements. However, it was recently shown that NO and NO_2 may not be measured by the standard bag sampling method, since NO is converted to NO_2 within minutes in the given bag conditions. Thus, these species need to be detected by an adequate online measurement method.
Reliable NO and NO_2 emission factors of different modern vehicle categories (gasoline, diesel, Euro 3, Euro 4) are shown for different driving situations such as real-world driving, cold start and for the statutory test. NO_2 ratios within NO_x of up to 70% are recorded. These results are complemented by particle data.

1 INTRODUCTION
Emissions of nitrogen oxides (NO_x) have again become topical in recent years in relation to air quality monitoring. Nitrogen oxides are an inevitable combustion product originating from gasoline and diesel engines, but also from industrial furnaces, heating installations and agricultural activities. Although levels of emitted nitrogen oxides (NO_x) have fallen sharply, roadside measurements indicate that concentrations of nitrogen dioxide (NO_2) appear to be stabilizing close to the future limit levels in Europe or even to be rising (Carslaw 2005, Carslaw and Beevers 2004(a),(b)). Besides its toxicity to humans, NO_2 also impacts on atmospheric ozone-forming chemistry. Higher source ratios of NO_2 to NO direct the atmospheric ozone chemistry to equilibria with higher ozone levels.
Formerly, it was assumed that NO_x emitted by vehicles typically consist of 95% nitrogen oxide (NO) and 5% nitrogen dioxide (NO_2). In the last few years, however, the increasing ratios of NO_2 to NO_x monitored near roadsides indicate that the share of NO_2 emitted by traffic has changed. This rise in the ratio of NO_2 to NO_x parallels the implementation of oxidation catalytic converters in diesel vehicles. These converters oxidise carbon monoxide and hydrocarbons originating from imperfect combustion in the engine, but may also convert NO to NO_2 at certain temperature conditions. In addition, more and more diesel cars are equipped with particle filter systems that employ NO_2 to oxidise trapped soot. This NO_2 is intentionally generated from NO in the precatalytic converter, but not controlled. Excess NO_2 may thus escape from the system as tailpipe emissions. Consequently precise measurement of vehicle emissions of NO and NO_2 has become necessary.
Measuring NO and NO_2 accurately in emission laboratories is not a standard problem though (Gense 2006, Weilenmann 2005). The standard measurement procedure, where a sample of diluted exhaust gas is stored in bags during the test run and subsequently analysed, is inappropriate. The bag's surface area allows NO to oxidise within minutes to NO_2 at room temperature and thus prevents accurate measurements. Consequently, measurements need to be executed online. A small sample of exhaust gas is analysed immediately (typically at 1 Hz or even 10 Hz) during the test run and the resulting signal patterns are integrated over time to gain meaningful values. The sample lines have to be heated because NO_2 is hydrophilic and may be solved in the condensed steam of the exhaust. In this regard, exhaust gas dryers positioned upstream of the analyser also represent a possible source of error.
Note that there are no standard analysers for NO_2. In regulated NO_x measurements only NO is measured directly using chemiluminescence detection (CLD). Converters placed in front of the CLD convert NO_2 to NO to permit its detection. Thus, NO_2 can be estimated by taking the difference of the measured signal traces from two comparable CLD devices, whereas one of which omits the NO_2-conversion. However, this is only an indirect determination of NO_2 and needs to be validated.
Furthermore it should be noted that NO_x as defined by regulations has the molar mass of NO_2. Thus, comparisons of NO to NO_2 or their ratios to NO_x have to be made on a concentration basis or by previously carrying out a mass correction. The true values of NO_x in grams per kilometre, resulting from the respective sum of NO and NO_2, are lower than the values for regulated NO_x.
In this paper, emission values of NO, NO_2, and NO_x of current car fleets are presented for real-world driving situations such as urban, rural and motorway driving, for cold start and for the statutory test. The vehicles are grouped according to their combustion principle and statutory category: gasoline Euro 4 (G4), diesel Euro 3 (D3) and Euro 4 (D4). Diesels cars with OEM particle filters (PF) are discussed as a separate group (D4 PF), since NO_2 here is intentionally formed in the precatalytic converter of some of these systems to oxidise particles in the trap. NO_2 has been measured according to the technique mentioned above and cross-checked

with accurate chemical ionisation mass spectrometry (CI-MS) running in parallel. The data are consequently presented in [g/km] true weight.

2 METHODOLOGY

Three samples of passenger cars for different combustion principles and statutory categories have been considered for the experimental investigation, cf. Table 1. The diesel cars of statutory category Euro 4, equipped with an OEM particle filter, are grouped separately. The car sample has been selected in order to match the Swiss fleet distribution of the single vehicle classes at the time of selection.

	sample	type	category	mass [kg]	displ. [cm^3]	power [kW]	mileage [km]
G4	17	gasoline	Euro 4	1334	2039	102	54519
D3	5	diesel	Euro 3	1604	2175	96	57014
D4	7	diesel	Euro 4	1476	1848	87	56278
D4 PF	3	diesel	Euro 4	1495	2327	113	41419

Table 1. Main characteristics of the considered car samples (physical specifications are average values)

The measurements were executed on a chassis dynamometer test bench using appropriate roller settings for the driving resistance of each car where available. Other settings were applied according to European Council Directive 70/220/EEC for passenger cars. A vehicle payload of 100 kg was considered.

The different driving situations were simulated by appropriate driving cycles. The CADC cycle includes representative urban, rural and motorway driving patterns derived within the European research programme ARTEMIS (André 2004). The IUFC15 cycle (André 1999) is most suitable to investigate the cold start effect on vehicle emissions, as it consists of 15 repetitions of a real-world urban driving pattern equally divided into three sections. The statutory cycle NEDC was also considered.

The accurate measurement of NO_2 involves both adequate sampling and analysing methods. Sampling of exhaust gas can be undertaken in four different ways. The regulatory procedure stipulates that the entire vehicle exhaust is sufficiently diluted with ambient air in order to prevent condensation of the steam contained in the exhaust when cooling down to ambient temperatures. A sample of the diluted exhaust is then collected in a tedlar bag during the single cycle sections and analysed after the test run is finished. It has been shown that NO oxidises to NO_2 in these bag conditions before the sample is analysed (Gense 2006, Weilenmann 2005), which eliminates this procedure for the desired investigation. Online measuring of the diluted exhaust could be considered as a way out. But the delay time of the diluted exhaust to be analysed, typically 10 to 20 seconds, is too long to avoid the oxidation mentioned. These delay times can be shortened using a small-scale dilution system to directly dilute only a sample extracted out of the raw vehicle exhaust. The authors have no experience of this method; however, it shows no benefit in analysing the exhaust sample directly without diluting. Therefore the exhaust sample needs to be kept above condensation temperature (typically 190°C) or needs to be dehumidified before analysis. When dehumidifying, the loss of water must be taken into account for the total exhaust volume flow calculation needed to process concentrations to absolute values. A loss of NO_2 dissolved in liquid water also has to be avoided, and dry dehumidification is thus to be performed, i.e. without having liquid water in contact with the exhaust gas.

There are various options for analysing NO_2. Chemiluminescence detectors (CLD) are the standard systems used to measure NO. Regulated NO_x emissions are collected when the detector is preceded by a converter unit that converts NO_2 to NO. These converters typically feature large surface areas of carbon where NO_2 reacts to NO and CO and operate at temperatures between 200 and 300°C. NO_2 concentrations can therefore be determined by taking the difference between two CLD signal traces, whereas one of which omits the NO_2-conversion. But ammonia in the exhaust, as appears for vehicles with SCR-DeNO_x systems or gasoline engines, may react with NO and NO_2 to N_2 and H_2O and distort the desired output. Measuring NO_2 with CLD analysers therefore requires validation by an independent method. Chemical ionisation mass spectrometry (CI-MS) represents a convenient measuring method thanks to its accuracy and lack of cross-sensitivities to NO and NO_2. It is not employed directly, however, because it requires precise calibration in short intervals and features fairly long measurement periods. Fourier transform infrared spectroscopy (FTIR) methods typically reach their detection limit in test bench operation and additionally show interference by water. Non-dispersive ultra-violet (NDUV) analysis appears to be a promising measuring method, but no operating experience for the desired investigation is known to the authors at present.

The concentration profiles of NO and NO_2 obtained in the measurements are computed to absolute values in [g/km] using the total volume flow of the exhaust and the molar masses of the single substances. The volume flow is corrected to take account of losses caused by sampling and dehumidifying of the measuring devices employed. The signal traces recorded are corrected in a post process regarding time and mixing delay of the analysis setup (Ajtay 2006). Note that the absolute values for nitrogen oxides given below correspond to the sum of NO and NO_2 derived from the measurements and form the basis for the ratios of the two substances.

3 EXPERIMENTAL RESULTS

The main results of the experimental investigation are shown in Figure 2 to Figure 4, where the averages and standard deviations of absolute NO and NO_2 emissions recorded with CLD measurements, cf. Chapter 2, are displayed together with the sum of both substances for each vehicle class and driving cycle. The resulting ratios of NO and NO_2 to their sum are also shown. Note that the sometimes rather high standard deviations are to be attributed to the selection of the car samples, which were to be representative of the Swiss car fleet and thus feature a wide range of makes and mechanisations.

It can be stated in general that absolute emissions of NO and NO_2 are mostly more pronounced in the measured real-world cycles than in the statutory cycle. Improvements in absolute emissions of nitrogen oxides can be observed from sample D3 to D4. The vehicles equipped with a particle filter, however, show higher emissions of nitrogen oxides that are mainly composed of NO_2. In contrast, the gasoline car sample G4 emits by far the lowest amounts of nitrogen oxides, which almost only consist of NO.

The measuring method of taking the difference between two CLD signal traces here reaches its performance limit, see Figure 1. The noise of the detector is dominant for very low concentrations of NO_2. In accordance with the respective CI-MS measuring data, cf. Figure 1, NO_2 emissions have been set to zero in these cases.

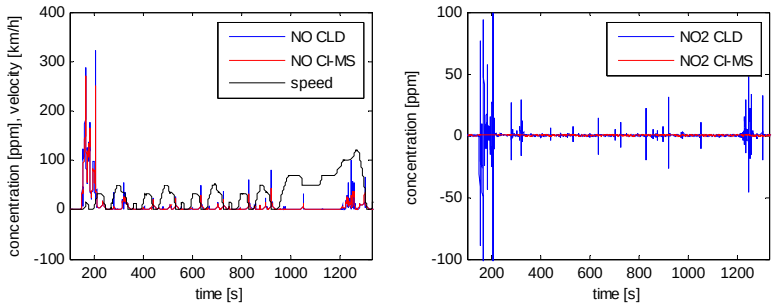


Figure 1. Variations in NO and NO_2 concentrations recorded by CLD and CI-MS devices in one NEDC cycle

Emissions of NO_2 are thus mainly of interest for diesel cars. The sample D3 features ratios of NO_2 of about 15% to 40% and the shares for the sample D4 range from 15% to 50%. A notable increase in the share of NO_2 can be observed for car sample D4 PF, with values of between 35% and 70%. The rise in the share of NO_2 during the cold start tests with the IUFC15 cycle indicates that the formation of NO_2 is enhanced when the light-off temperature of the installed oxidation catalytic converter is reached.

Regarding particle emissions, an increase is visible from sample D3 to D4, cf. Figure 5. Efforts in lowering NO_x emissions may have led to this rise. Note that 5 of the 7 cars in sample D4 even exceed the respective limit values. It appears that only the adoption of particle filter systems allows a substantial reduction in particle emissions.

4 CONCLUSIONS

The present experimental investigation shows that modern gasoline cars feature very low NO_x emissions that have a maximum share of 3% NO_2 or even less. Diesel cars without particle filters have improved regarding total emissions of NO_x, but show increased shares of NO_2 of 10% to 50% without a reduction in their particle emissions. In contrast, modern Diesel cars equipped with OEM particle filters emit more NO_x than vehicles of earlier statutory categories and exhibit relative contents of NO_2 between 35% and 70%. In addition, it turned out that the measuring method for determining NO_2 based on CLD measurements is inappropriate for very low NO_2 concentrations.

5 ACKOWLEDGEMENTS

The authors thank the Swiss Federal Office for the Environment (FOEN) for principally funding the study.

6 REFERENCES

Ajtay, D. 2006. Modal Pollutant Emissions Model of Diesel and Gasoline Engines, Dissertation No. 16302, 114pp, Swiss Federal Institute of Technology, Switzerland.

André, M. 2004. The ARTEMIS European driving cycles for measuring car pollutant emissions. Science of the Total Environment 334-335, 73-84.

André, M., Hammarström, U., Reynaud, I. 1999. Driving Statistics for the assessment of pollutant emissions from road transport. INRETS Report No. LTE9906, Bron, France.

Carslaw, D. C. 2005. Evidence of an increasing NO_2/NO_X emissions ratio from road traffic emissions, Atmospheric Environment 39, 4793-4802.

Carslaw, D. C., Beevers, S. D. 2004(a). New Directions: Should road vehicle emissions legislation consider primary NO_2, Atmospheric Environment 38, 1233-1234.

Carslaw, D. C., Beevers, S. D. 2004(b). Investigating the potential importance of primary NO_2 emissions in a street canyon. Atmospheric Environment 38, 3585-3594.

Gense, R., Vermeulen, R., Weilenmann, M., McCrae, I. 2006. NO_2 emissions from passenger cars. 2nd Conf. Environment & Transport – Transport and Air Pollution, Reims, France.

Weilenmann, M., Saxer, C., Forss, A.M., Heeb, N., Stilli, J., Novak, P. 2005. Time-resolved raw gas measurements of NO and NO_x for diesel and gasoline vehicles. 14th Symposium Transport and Air Pollution, Graz, Austria

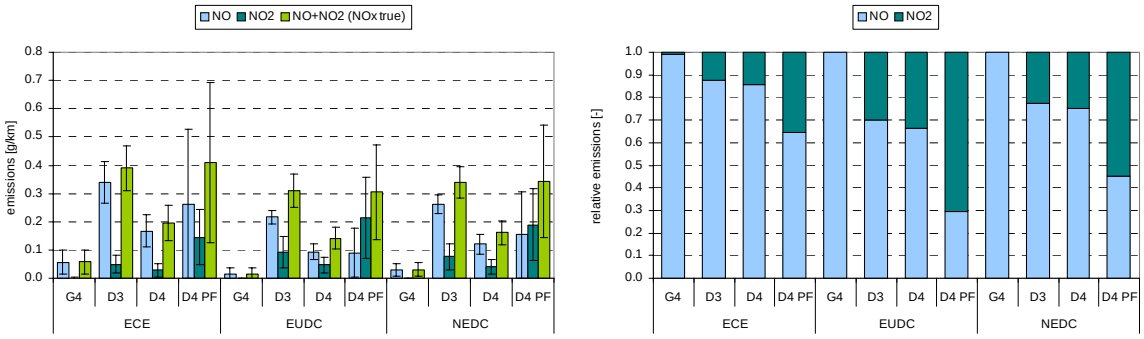


Figure 2. NO and NO_2 emissions of the different car samples in the statutory cycle NEDC

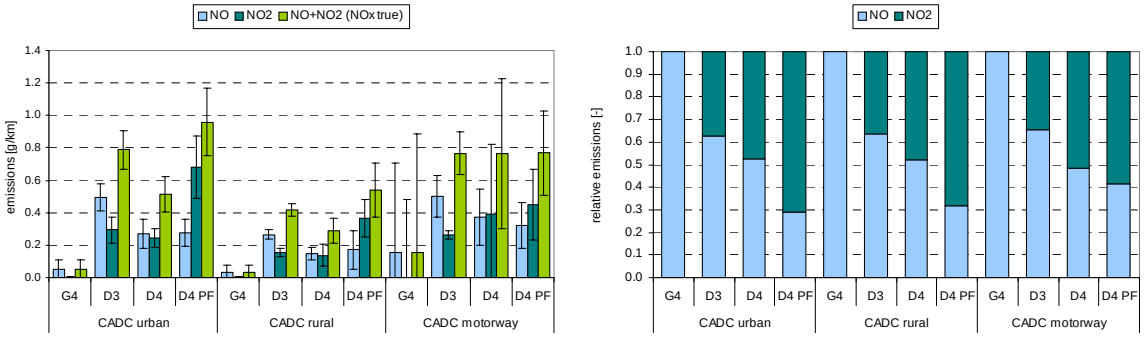


Figure 3. NO and NO_2 emissions of the different car samples in the real-world cycle CADC

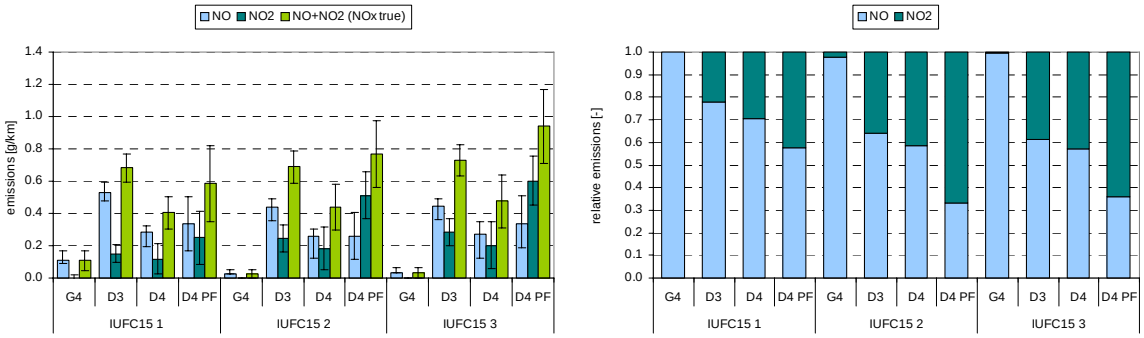


Figure 4. NO and NO_2 emissions of the different car samples in the real-world cold start cycle IUFC15

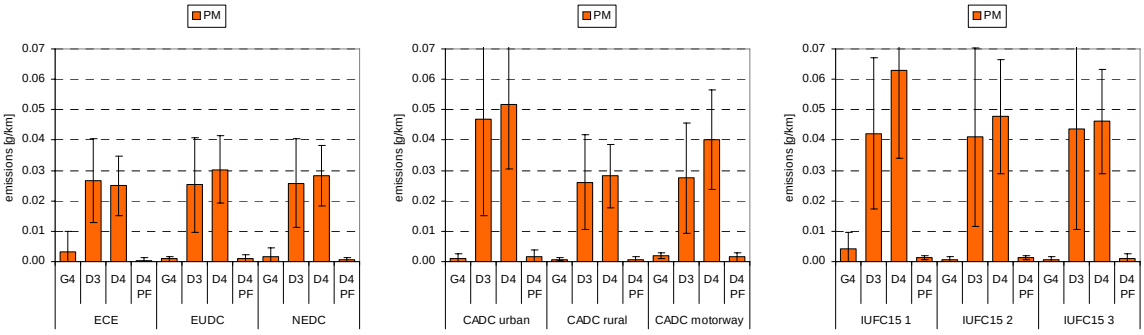


Figure 5. Particle mass emissions of the different car samples in the driving cycles considered

Proceedings of the 6th International Conference on Urban Air Quality
Limassol, Cyprus, 27-29 March 2007

COLD START EMISSIONS OF PASSENGER CARS AT DIFFERENT LOW AMBIENT TEMPERATURES

Jean-Yves Favez[1] and Martin Weilenmann[1]
[1]Empa, Swiss Federal Laboratories for Materials Testing and Research, Laboratory for Internal Combustion Engines; Ueberlandstrasse 129, CH-8600 Duebendorf, Switzerland.
Phone: +41 44 823 46 22, fax: +41 44 823 40 44, jeanyves.favez.favez@empa.ch

ABSTRACT

The emissions of modern passenger cars are usually reduced by catalysts. But since catalysts require a certain temperature (above 200°C) to work fully efficiently the emissions are significantly higher during the cold start, i.e. the warm-up phase of the car. The duration of this period and the emissions produced during it depend on the ambient temperature as well as on the initial temperature of the car's systems.
The additional emissions during a warm-up phase, called cold start extra emissions, are mostly assessed by means of emission measurements at an ambient temperature of 23 °C. But in many European countries the average ambient temperatures are frequently below 23 °C. This fact calls for emission measurements at lower temperatures in order to model and assess cold start emissions for real-world temperature conditions.
This present work investigates on the influence of regulated pollutants and CO_2 emissions of recent gasoline and diesel car models (Euro-4 legislation) at different ambient temperatures, i.e. 23, -7, and -20 °C. For gasoline cars, it turns out that the major part of the CO and HC total emissions are due to cold start extra emissions. Moreover, the cold start emissions increase considerably at lower ambient temperatures. In contrast, cold start emissions of diesel cars are significantly lower than of gasoline cars. In the framework of this study we furthermore present a survey of the cold start emissions evolution as a function of different car generations (pre-Euro-1 to Euro-4 legislations).

1 INTRODUCTION

The analysis of additional emissions during the warm-up phase, called the cold start extra (or excess) emissions, has gradually gained in importance in order to improve emission models and thus emission inventories. An exhaustive survey of the researches carried out in the past concerning cold start emissions is given in the report by (André and Joumard, 2005). In general, the research on the characterisation of cold start emissions focuses on following 5 topics: i) technology or emission standard (Euro-0 … Euro-4), ii) average vehicle speed, iii) ambient temperature, iv) travelled distance and v) engine stop time (also called parking time). In this present work we focus on low ambient temperature.
Many data are available for the standard cold start extra emission assessment at an ambient temperature of (or around) 23°C. But since the average temperature in Europe and especially in Switzerland is distinctly below 23°C this standard assessment procedure does not suffice in order to get a representative emission estimation. Furthermore, for most pollutants the evolution of cold start extra emissions as a function of ambient temperature is not linear (Weilenmann 2005). Thus, it is not sufficient to estimate cold start emissions at a single representative average temperature. In fact, estimations for different temperature conditions, e.g. winter conditions, have to be considered separately. To meet this necessity it has become a common task to additionally establish cold start extra emissions on a representative subset of all assessed cars at (or around) ambient temperatures of -7°C and -20°C. The objective is to develop a model which allows the estimation of cold start extra emissions at low ambient temperature as a function of the standard cold start extra emission at 23°C.
In this paper a summary of the two most common extra emissions estimation methods is presented. We then present recent cold start extra emission results for Euro 4 gasoline and diesel passenger cars. The focus is set on the regulated pollutants (CO, HC, NO_x and PM) and CO_2 assessed at 23, -7 and -20°C. Finally, we give a survey of the extra emissions evolution as a function of temperature and different passenger car generations, i.e. diesel Euro-2 and -4 legislations and gasoline pre-Euro-1 (denoted as Euro-0), Euro-3 and -4 legislations.

2 EXPERIMENTAL PROGRAM

An accurate estimation of cold start extra emissions is based on measurements of emissions by means of a repetitive driving cycle. For real-world emission inventories it is important to use test cycles which are as close as possible to real-world on-road driving. Additionally, we assume that most car journeys start in an urban environment. The most appropriated cycle for these purposes is the IUFC15 cycle which is composed of 15 "INRETS urbain fluide court" cycle (IUFC). One IUFC cycle has a length of 0.999 km, a duration of 189 s and an average velocity of 19 km/h. In what follows a single IUFC cycle is referred to as a subcycle of the repetitive IUFC15 cycle.
The common and widely accepted procedure for estimating cold start extra emissions is to apply one of the following estimation methods:

1. Subcycle analysis method :
   The repetitive cycle has to be separated into two parts: the cold phase and the hot phase parts. Thus,

we first have to determine which subcycles belong to the cold phase. This separation can be effectuated graphically "by hand" by analysing the total subcycle emissions as a function of the chronological succeeding subcycles which corresponds to a discretized time line. Figure 1 illustrates a cycle with 15 subcycles, as e.g. the IUFC15 cycle. In this case the 7th subcycle can be considered as the last subcycle of the cold phase referred to as n_c. A method developed at INRETS, the so-called standard deviation method, permits to compute n_c. In (André and Joumard, 2005) a detailed description of this method is presented. Once n_c is known the cold start extra emission is given by

$$EE_{cold} = E_{cyc} - E_{hot} = \sum_{i=1}^{15} E(i) - \frac{15}{15-n_c} \sum_{i=n_c+1}^{15} E(i),$$

where $E(i)$ is the total emission of subcycle i, E_{cyc} is the total emission of the cycle and E_{hot} is the sum of the hot emission part of the cycle.

In general, since the emissions of each subcycle have to be estimated, equipments with instantaneous emission acquisition are required. But since some laboratories measure emission factors by means of bags only, following method is proposed.

2. Bag analysis method:
At EMPA a complete cycle is subdivided into 3 bag measurements. In the case of an IUFC15 the total emission of subcycles 1-5, 6-10 and 11-15 correspond to the bags 1, 2 and 3, respectively. By assuming that the cold phase ends before the start of the third bag (first 10 subcycles) the cold start extra emission is given by

$$EE_{cold} = E_{bag1} + E_{bag2} - 2E_{bag3}.$$

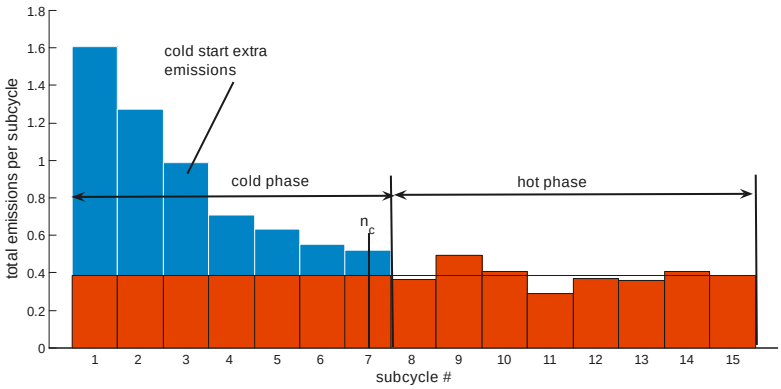


Figure 1. Emissions evolution as a function of subcycle. Separation of the cycle into a cold and a hot phase.

Notice that the evolution of emissions as a function of subcycles can show three distinctly different shapes. The first shape, which is the most common one, is depicted in Figure 1. The second shape, starts as in Figure 1, decreases until a minimum emission level, which is below the hot phase emission level, and finally increases gradually until the constant hot phase emission is reached. The last shape starts with a lower emission level than the hot phase emission and gradually increases until the constant hot phase emission is reached. Thus, the estimated cold start extra emissions can be negative for emission shapes of type 2 and is always negative for type 3 emission shapes. These two cases occur mainly for NO_x emissions, since at the start the engine is cold and thus less NO_x is produced as in a fully warmed up engine.

The test fleet is composed of vehicles which reflect the Swiss fleet distribution of the single vehicle classes at the time of selection. The cars are obtained from voluntary private owners and are not serviced before the test. In Table 1 the main characteristics of the considered test fleets are listed. For the Euro-4 diesel categoryytwo cars are equipped with catalysed soot filters and one car with a fuel borne catalyst filter.

	# of vehicles	type	category	mass [kg]	displacement [cm^3]	power [kW]	mileage [km]
PG0	6	gasoline	Euro-0	1143	1906	80	124336
PG3	8	gasoline	Euro-3	1276	1812	90	27669
PG4	6	gasoline	Euro-4	1289	2016	94	46497
PD2	6	diesel	Euro-2	1401	1972	76	67327
PD4	6	diesel	Euro-4	1459	1981	94	47076

Table 1. Main characteristics of the considered test fleets (physical specifications are average values)

In what follows we will focus on the extra emissions of the recent gasoline and diesel Euro-4 campaigns. A detailed analysis of the anterior campaigns is given in (Weilenmann 2005 and Stettler 2004).

For the cold start emission estimations of the gasoline test fleet the subcycle method has been applied. The reason for this is that gasoline vehicles in general exhibit strong emission variations during the hot emission phase. Under such circumstance it has been shown in (Favez 2006) that the subcycle method provides the most accurate results.
On the other hand, diesel vehicles show remarkable small emission variations during the hot phase. Thus, both the subcycle and the bag methods provide similar results. Concerning the diesel test fleet the bag method has been opted as the method of choice since the mass measurement of the particulate matter mass is solely available on the scale of bags.
The cold start extra emission for the anterior campaigns have all been computed by means of the bag method, as presented in (Stettler 2004).

3 EXPERIMENTAL RESULTS

The cold start extra emissions for the gasoline Euro-4 test fleet is illustrated in Figure 2. There is a clear trend of higher CO and HC emissions when temperature decreases. At -20°C the cold start extra emissions of CO and HC are up to 15 and 35 times higher than at 23°C, respectively. In contrary, no evident trend can be detected for NO_x emissions, a result that has already been observed for gasoline Euro-3 vehicles (Weilenmann 2005). While the extra fuel consumption (not shown in the figure) increases almost linearly as a function of decreasing temperature, the CO_2 extra emissions stagnate or even slightly decrease between -7 and -20°C. Thus, at very low temperatures the amount of partially and non-combusted fuel increases disproportionately. This observation is confirmed by the higher gradient of CO and HC emissions between -7 and -20°C.
Figure 3 illustrates the cold start extra emissions for the diesel Euro-4 test fleet. For CO emissions there is a clear upwards trend when temperature decreases, while no trend can be detected for HC emissions. Vehicle PD4-6 shows disproportional extra emissions at -20°C which is due to engine start problems. As opposed to the gasoline cars, there is an evident increase of NO_x emissions as a function of decreasing temperature. The reason for this effect is not obvious so far. The extra fuel consumption and CO_2 emissions increase almost linearly as a function of decreasing temperature. At -20°C vehicle PD4-3 suddenly switches after subcycle 4 in a fuel-enriched mode which is held until the end of the test. This results in a distinct increase of CO_2 emissions during the hot phase and thus leads to an unexpected low cold start extra emission estimation. So far it is not clear if this effect is due to a control procedure: i) either for regenerating the particulate filter or ii) to ensure a faultless functioning of the engine and the aftertreatment systems at this very low temperature.
Figure 4 illustrates the overlook of cold start extra emissions as a function of different passenger car generations. For each generation the average of extra emissions is computed. Because of the singular behaviour of vehicles PD4-3 and PD4-6 at -20°C, i.e. fuel-enriched mode and engine start problem, respectively, we omit this data for the average computation in order to prevent a biased representation of the fleet. In general, the cold start extra emissions are lower for cars equipped with more recent technologies. The CO and HC extra emissions for diesel cars are distinctly (about a factor of 10) lower than for gasoline vehicles. There is a high CO and HC extra emission difference between gasoline vehicles without catalysts (Euro-0) and newer gasoline cars, while no major improvement from Euro-3 to Euro-4 cars can be observed. As for diesel vehicles, the Euro-0 gasoline cars show a clear trend for higher NO_x extra emissions when temperature decreases. This is not the case for gasoline cars equipped with three-way-catalysts (Euro-3 and -4) for which NO_x extra emissions seem not to be sensitive to temperature changes. Concerning the CO_2 extra emissions, the most striking feature is the stagnation for gasoline Euro-4 cars at very low temperature, whereas for all other car generations and technologies an increase is the common characteristic. The diesel cars without particulate filters clearly tend to exhaust a higher amount of particulate matter when temperature decreases, specifically for diesel Euro-2 cars at -20°C. For filter equipped vehicles no trend can be stated since the exhausted particulate mass is clearly below the detection limit of the measurement equipment.

4 ACKOWLEDGEMENTS

The authors thank the Swiss Federal Office for the Environment (FOEN) for mainly funding the study.

5 REFERENCES

André J-M. and Joumard R. (2005): Modelling of cold start excess emissions for passenger cars. INRETS report, n° LTE 0509, Bron, France, 239 p.

Favez J-Y., Weilenmann M., Stilli J. 2006. Cold start extra emissions as a function of engine stop time: The evolution during the last 10 years, Proceedings of the 2nd Environment and Transport Conference, Reims, June 2006

Stettler P., Weilenmann M., et al. 2004: Messungen 01-02, Benzinpersonenwagen Euro-0 und Euro-3 sowie Dieselpersonenwagen Euro-2, Untersuchungsbericht Nr. 202114, EMPA, Überlandstrasse 129, 8600 Dübendorf

Weilenmann, M. 2005. Regulated and nonregulated diesel and gasoline cold start emissions at different temperatures, Atmospheric Environment 39, 2433-2441.

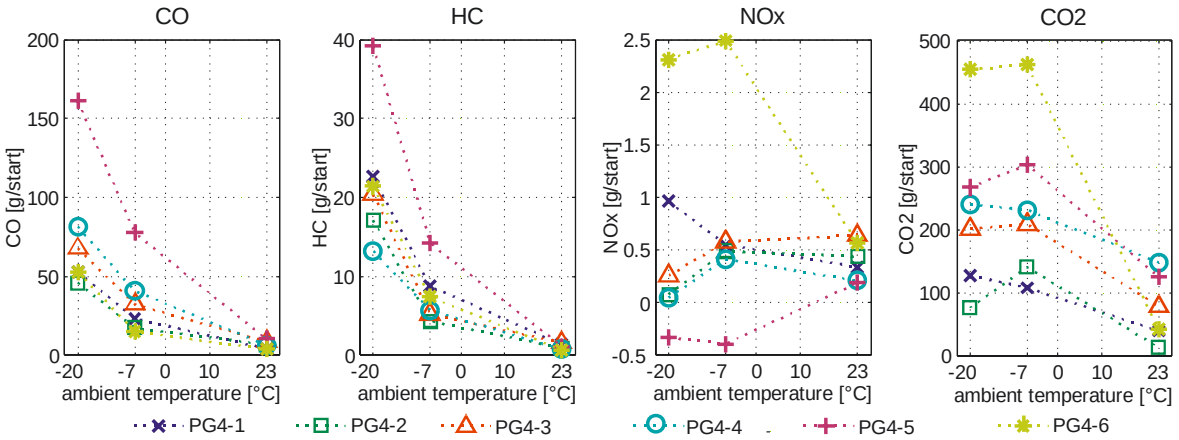


Figure 2. Cold start extra emissions as a function of ambient temperature for the gasoline Euro-4 test fleet

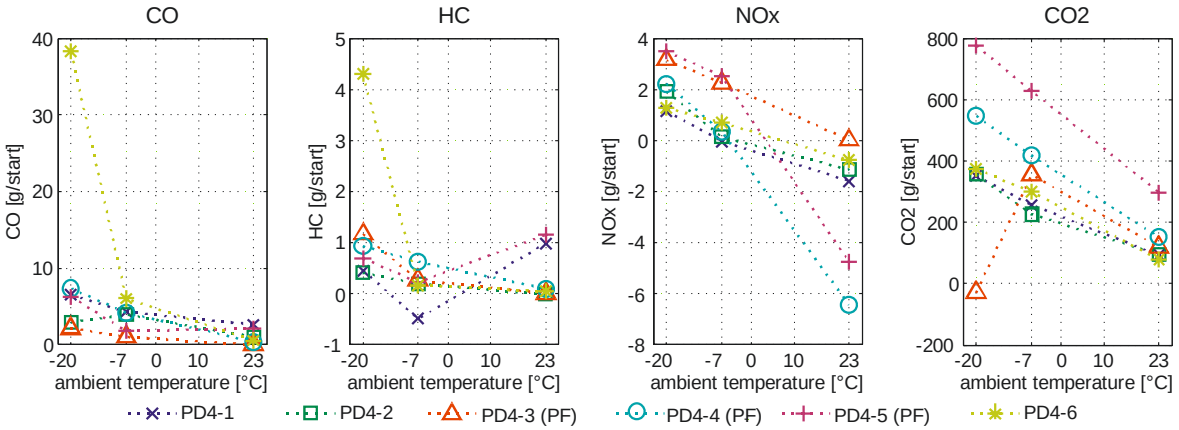


Figure 3. Cold start extra emissions as a function of ambient temperature for the diesel Euro-4 test fleet

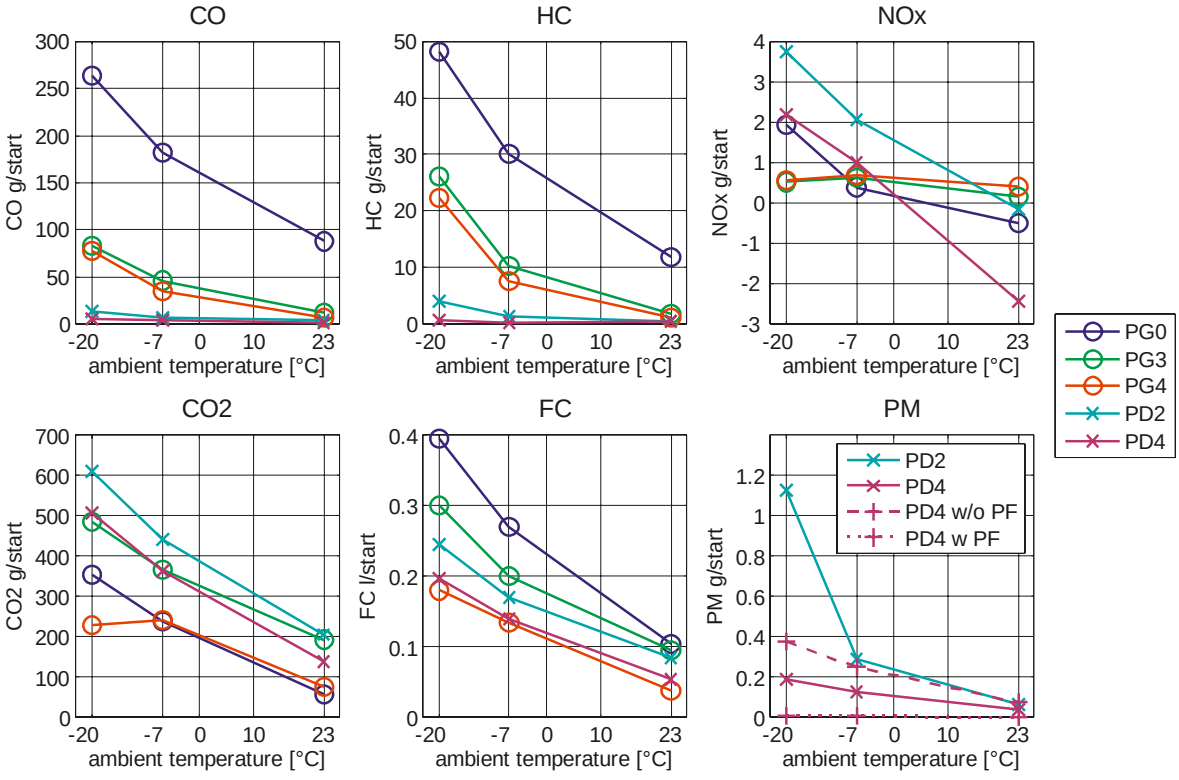


Figure 4. Comparison of the average cold start extra emissions of different passenger car generations
PG0: gasoline Euro-0, PG3: gasoline Euro-3, PG4: gasoline Euro-4, PD2: diesel Euro-3, PD4: diesel Euro-4

Proceedings of the 6th International Conference on Urban Air Quality
Limassol, Cyprus, 27-29 March 2007

THE MOBILE LABORATORY "SNIFFER" FOR NON-EXHAUST EMISSION MEASUREMENTS: VALIDATION OF THE SYSTEM AND THE FIRST RESULTS

Pirjola, L.[1,2,*], Kupiainen, K.[3,4] and Tervahattu, H.[3]

[1]Helsinki Polytechnic, Department of Technology, P.O. Box 4020, FIN-00099 Helsinki, Finland
[2]University of Helsinki, Department of Physical Sciences, P.O. Box 64, FIN-00014 Helsinki, Finland
[3]Nordic Envicon Oy, Koetilantie 3, FIN-00790 Helsinki, Finland.
[4]University of Helsinki, Department of Biological and Environmental Sciences, P.O. Box 56, FIN-00014 University of Helsinki

[*]liisa.pirjola@stadia.fi , phone: +358-9-310 83245, fax: +358-9-310 83550

ABSTRACT

This paper describes the design of a mobile system SNIFFER to measure non-exhaust particulate emissions from road surface. Dust sample is sucked from behind the left tire of SNIFFER into a conical inlet. PM_9 is measured by the particle mass monitor TEOM and $PM_{2.5}$ by ELPI. The conical inlet was shown to catch most of the road dust emission plume behind the tire. Particle losses in the inlet lines were around 26%. The SNIFFER signal was converted to emission factor (g km^{-1}) based on the flux tower measurements using upwind/downwind technique as well as on-board measurements. The ratio of emission factor and SNIFFER signal was 0.39. The city route measurements showed that in Finland street dust levels are especially high during spring due to the use of antiskid methods (street sanding, studded tires), but a clear decreasing trend in PM_{10} and $PM_{2.5}$ can be observed until the end of May.

1. INTRODUCTION

Recent toxicological and epidemiological studies have associated high particulate concentrations (PM) in urban air with increased morbidity such as respiratory symptoms, lung cancer and cardiovasculare diseases, and with increased mortality (e.g. Pope et al., 2002 ; Saxon et al., 2005). Also recentrly reported is epidemiological evidence of effects of coarse non-exhaust airborne particles on health (Brunekreef and Forsberg, 2005).

Non-exhaust particles are mainly abrasion products originating largely from interaction of the road surface and tire. An important source is also particles that are re-suspended from surfaces, e.g., due to vehicle induced turbulence or tire shear. In Northern areas, e.g., in Scandinavia, street dust levels are especially high during spring due to the use of antiskid methods, like street sanding and studded tires.

This work describes the design and validation of a mobile system SNIFFER to measure non-exhaust particulate emissions from street/road surface. The results from the first city measurements are discussed. Also the correlation of the SNIFFER signal and the emission factor measurements based on an upwind/downwind technique is presented.

2. METHODOLOGY

The mobile laboratory SNIFFER was first developed to measure traffic emissions under real driving conditions as well as exhaust emissions of an individual vehicle with the chasing method (Pirjola et al., 2004a; 2004b). In 2005 the measurement set up was extended to include also measurements of non-exhaust particles during a Finnish national project VIPEN (Vehicle Induced Particulate Emissions from Non-exhaust Sources). The instrumentation is set in a Volkswagen LT35 diesel van with a length 5585 mm, width 1933 mm, height 2570 mm, and max total weight 3550 kg.

Dust sample is sucked from behind the left tire through a conical inlet with the surface area of 0.20 m x 0.22 m into a vertical tube with the diameter of 0.1 m. The lower edge of the conical inlet is 7 cm above the road surface and the upper edge is as high as the geometry of the fender of the wheel allows. The width of the inlet is around 2 cm less than the width of the tire or 1 cm less from each side, and the distance of the inlet from the tire is 5 cm (Fig. a). The tube runs through the rear part to the top of the van (Fig. 1b).

A constant flow rate of 1600 lpm is provided by an electric engine located on the roof of the vehicle. A sampling air branch-off (Fig. 1b) into the tube of 0.025 m diameter was constructed for the particle mass monitors TEOM (Tapered Element Oscillating Microbalance, Series 1400A, Rupprecth & Patashnick) and

Figure 1. a) The conical inlet behind the left tire of Sniffer. b) The sampling system.

ELPI (Electrical Low Pressure Impactor, Dekati Ltd) allowing isokinetic sampling. The total flow rate is 13 lpm (3 lpm for TEOM and 10 lpm for ELPI), and a sampling cyclone (SAC-65, Dekati) with a 9.2 µm cutoff is used (Fig. 1b). This TEOM operates at 303 K temperature so evaporation of semivolatile aerosol material (such as ammonium nitrate and certain organic compounds) is not a problem. The TEOM was installed to save 30 s running average mass concentration every 10 s whereas ELPI with the electrical filter stage enables real time particle number concentration and size distribution (1 s time resolution) in the size range of 7 nm – 10 µm (aerodynamic diameter) with 12 channels (Keskinen et al., 1992). Thus this installation allows the TEOM to monitor PM_9 whereas the ELPI is used to measure mass fractions $PM_{2.5}$, and for example PM_1 and $PM_{0.1}$, as well as particle number and mass size distributions. In this work we have eliminated the mass concentration of the exhaust particles and calculated $PM_{2.5}$-$PM_{0.6}$ by assuming the particle density of 2000 kg m^{-3}.

Sniffer also provides the measurements of gaseous concentrations such as carbon monoxide CO (Model CO12M, Environnement S.A.), nitrogen monoxide NO, nitrogen oxides NOx = NO+NO_2 (Model APNA 360, Horiba) as well as carbon dioxide CO_2 (Model VA 3100, Horiba). Particle number concentration and size distribution are measured by the other ELPI using the inlet in front of the van. These ELPI recorders are also used in estimating the background $PM_{2.5}$.

Sniffer has a weather station on the roof at 2.9 m height providing meteorological parameters. Relative wind speed and direction are measured with an ultrasonic wind sensor (Model WAS425AH, Vaisala). Temperature and relative humidity are measured with temperature and humidity probes (Model HMP45A, Vaisala). Additionally, a global position system (GPS V, Garmin) saves the vans speed and the driving route. Also available is a video camera in the cab to record the traffic situations.

3. RESULTS AND DISCUSSION

3.1. Validation

The objective of the sampling was to catch the most of the particles in the plume originated from the tire and road interaction, and to record the average values of the whole plume instead of recording concentrations only at one fixed location in the variable plume. The particle losses for $PM_{9.2}$ in the sampling tubes were calculated to be 26% (Willeke and Baron, 1993.

We constructed a rack at a distance of 5 cm from the left back tire of SNIFFER to carry out 2-dimensional road dust sampling tests in a grid which covered an area of 305 mm x 240 mm with 20 grid points at five vertical and four horizontal lines. The vertical lines were located in the middle of the tire, 10 mm inside both edges of the conical inlet, and 50 mm outside both edges. The horizontal lines were located at the centre, the top and lower edges, and 20 mm below the conical inlet, ie. at 50 mm from the road surface. The samples were collected through a 10mm stainless steel tube to TEOM and ELPI.

The results indicated that the horizontal width of the conical inlet was enough but the vertical height should be larger because part of the plume was emitted below the inlet (Pirjola et al., 2007). However, 70 mm was the smallest distance from the road to prevent the inlet from touching the ground.

3.2. Emission factor

To evaluate the average road dust PM_9 emission factor (g km^{-1}) for SNIFFER we performed flux tower measurements based on an upwind/downwind technique presented by Moosmüller et al. (1998), Abu-Allahin et al. (2003) and Gertler et al. (2006). The measurements were performed on an asphalt field closed by other traffic in Helsinki on 9 and 11 October, 2006. The instruments of SNIFFER (TEOM and ELPI) were moved to a downwind tower and the inlets were installed at the altitude of 1.37 m. The measurements were repeated at altitudes of 2.02 and 3 m. The location of the tower was changed from 2 m to 3.75 m and to 6 m from the lane edge. SNIFFER was passing the tower with the speed of 30 and 50 km h^{-1}. Each set of measurements were repeated at least five times. The background concentrations were measured at the beginning and after changing any parameter as well as the meteorological parameters.

Since the TEOM was too slow to follow the details of the PM_9 signal caused by SNIFFER, we first determine the PM_4 (diameter < 4 μm) emission factor for SNIFFER based on the ELPI results by the equation (1) (eg. Gertler et al., 2006).

$$EF_4(\text{g km}^{-1}) = \sum_{i=1}^{n} u_i(ms^{-1}) \cos\theta_i \Delta t_i(s) \sum_{j=1}^{4} c_{ij}(\mu g m^{-3}) \Delta z_j(m) \cdot 10^3 (km/m) \cdot 10^{-6} (g/\mu g) \qquad (1)$$

where u_i is the wind speed and θ_i the wind direction in respect to the road heading, Δt_i is the time over which the road dust signal appears at the measurement point, and Δz_i is the monitoring height. The road dust PM_4 concentration c_{ij} is calculated from the ELPI number concentrations, however, to eliminate the exhaust particles only the ELPI stages 8-11 corresponding to the particle diameter range of 600 nm – 4 μm were taken into account.

Next the emission factor PM_9 for SNIFFER was estimated from the measured ratio of PM_9/PM_4. For this purpose, also the instrumented SNIFFER was driving the same lane with a constant speed of 30 km h^{-1} or 50 km h^{-1}, and the average road dust PM_9 and PM_4 were calculated.

As a result, the ratio of the SNIFFER road dust PM_9 emission factor to the SIFFER signal was found to be around 0.38.

3.3. City route

The measurements were conducted in Helsinki, Finland, during springtime in 2005-2006 before, during and after street cleaning activities on a route located in urban environment. Figure 2 shows the average PM-concentrations over the whole route in 2006. $PM_{2.5}$ is 13-28% of PM_9. The results show clear decreasing trend, however, high concentrations after street cleaning were observed.

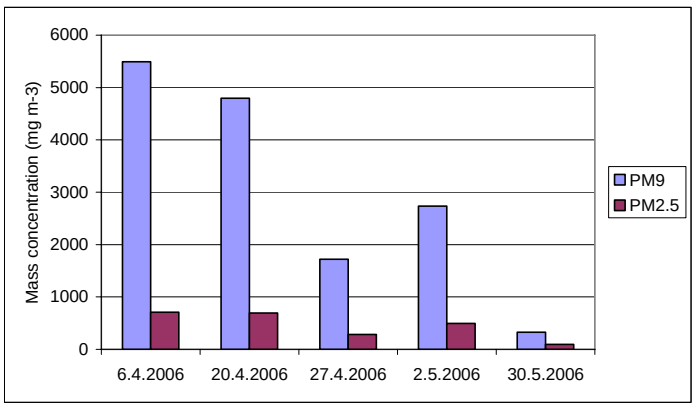


Figure 2. Average PM_9 and $PM_{2.5}$ concentrations in 2006 in Helsinki.

4. CONCLUSIONS

The mobile air quality research laboratory SNIFFER was further developed to measure non-exhaust particulate emissions from road surface. Dust sample is sucked from behind the left tire of SNIFFER into a conical inlet. PM_9 is measured by the particle mass monitor TEOM and $PM_{2.5}$ by ELPI. The conical inlet was shown to catch most of the re-suspended road dust plume. Particle losses in the inlet lines were around 26%.

The SNIFFER signal was converted to emission factor (g km^{-1}) based on the flux tower measurements using upwind/downwind technique as well as on-board measurements. The ratio of the PM_9 emission factor and SNIFFER signal found to be around 0.39.

The city route measurements showed that in Finland street dust levels are especially high during spring due to the use of antiskid methods, like street sanding and studded tires, but a clear decreasing trend can be observed for both in PM_9 and $PM_{2.5}$. $PM_{2.5}$ (exhaust particles were subtracted) was 13-28% of thePM_9.

5. ACKNOWLEDGEMENTS

The authors would like to thank the National Technology Agency of Finland (TEKES), the Helsinki Metropolitan Area Council, and Ministry of Environment, Finland for financial support.

6. REFERENCES

Abu-Allaban, M., Gillies, J.A., Gertler, A.W., Clayton, R., Proffitt, D. 2003. Tailpipe, resuspended road dust, and brake-wear emission factors from on-road vehicles. Atmospheric Environment 37, 5283-5293.

Brunekreef, B. and Forsberg, B, 2005. Epidemiological evidence of effects of coarse airborne particles on health. European Respiratory Journal 26, 309-318.

Gertler , A.W., Gillies, J.A., Pierson, W.R. 2000. An assessment of the mobile source contribution to PM10 and PM2.5 in the United States. Water Air and Soil Pollution 123, 203-214.

Keskinen, J., Pietarinen, K. and Lehtimäki, M., 1992. Electrical Low Pressure Impactor., *J. Aerosol Sci.,* **23**, 353.

Kupiainen, K., Pirjola, L. and Tervahattu, H. 2005. Mobile measurements of spring-time dust in Helsinki, Finland. Report Series in Aerosol Science, 77, 78-83.

Moosmüller, H., Gillies J.A., Rogers, C.F., DuBois, D.W., Chow. J.C:, Watson, J.G., Langston, R. 1998. Particulate emission rates for unpaved shoulders along paved roads. Journal of the Air and Waste Management Association 48, 174-185.

Pirjola, L., Parviainen, H., Hussein, T., Valli, A., Hämeri, K., Aalto, P., Virtanen, A., Keskinen, J., Pakkanen, T., Mäkelä, T., Hillamo, R. 2004. "Sniffer" – a novel tools for chasing vehicles and measuring traffic pollutants. Atmospheric Environment 38, 3625-3635.

Pirjola, L., Parviainen, H., Lappi, M., Hämeri, K. and Hussein, T. (2004b) A novel mobile laboratory for "chasing" city traffic. SAE-paper no 2004-01-1962.

Pirjola, L., Perhoniemi, P., Kupiainen, K., Tervahattu, H., Vesala, H. 2007. Mobile laboratory for measurements of road dust in Finland. To be submitted to Environmental Science and Technology.

Pope III CA, Burnett RT, Thun MJ, Calle EE, Krewski D, Ito K, Thurnston GD. 2002. Lung cancer, cardiopulmonary mortality, and long-term exposure to fine particulate air pollution. *American Medical Association* 287, 1132-40.

Saxon, A, Diaz_Sanchez, D. 2005. Air pollution and allergy: You are what you breathe. Nature Immunology 6, 223-226.

Willeke, K. and Baron, P.A. (1993). Aerosol Measurement: Principles, Techniques, and Applications. Van Nostrand Reinhold, New York.

EVALUATING AN URBAN EMISSIONS INVENTORY MODEL USING MULTI-REGRESSION AIR POLLUTION MAPS FROM EXTENSIVE MONITORING

S. Mesquita[1] , F. Ferreira[1], V. Gois[2], P. Torres[1], L. Nogueira[3], J. Monjardino[1], C. Almeida[3], H. Maciel[2]

1 Departamento de Ciências e Engenharia do Ambiente, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, Quinta da Torre, 2829-516 Caparica, Portugal

2 InventAr, R. Sarmento Beires 15-8E, 1900-410, Lisboa, Portugal

3 Comissão de Coordenação e Desenvolvimento Regional de Lisboa e Vale do Tejo, Rua Bramcamp, 7, 1250-048 Lisboa, Portugal

ABSTRACT

The inventory of air emissions for the city of Lisbon was recently subjected to significant improvements including a very detailed road traffic model and an air emissions spatial allocation model. This model was based on the identification of vehicles circulation from aerial photographic data, vehicle velocities from GPS on-vehicle monitoring, fuel sales and commuter's fluxes, and surveys for the characterization of the circulating fleet. In this paper, an approach to evaluate the spatial desegregation of the nitrogen oxides emissions using multi-regression models to relate emissions with air quality results from extensive passive diffusive sampling monitoring was developed. To incorporate the influence of all nearby emission sources in the spatial models, GIS techniques such as spatial buffering and data extraction were used. With this methodology it was possible to develop a model that explains more than 60% of the spatial variability of the nitrogen dioxide concentrations.

1. INTRODUCTION

An air emission inventory for a dense urban area such as Lisbon must be able to deliver a very detailed resolution. Therefore, it has to be based on a bottom-up approach, where traffic is allocated to each and every road link. Usually, as the case of Lisbon, actual traffic monitoring data is only available for the most important road links where traffic congestion is a major problem and therefore insufficient for inventory needs. Some approaches, such as the use of Traffic Network Flow Models that determine traffic demand using a matrix of Origin-Destination, require the development of surveys, which are usually resource consuming, while their uncertainty remain unknown unless their results are evaluated using field data. Another alternative and simple methodology, which can be used to develop a highly detailed spatial disaggregated inventory of air emissions from road transportation and area combustion sources, was developed by Gois et al, 2005. This new spatial methodology for emissions allocation, particularly road traffic fluxes and road traffic emissions is potentially very valuable when a substantial level of spatial detail is a requisite, with the advantage of being relatively inexpensive, and based in easily available information.

The spatial modeling of the long term air quality indicators in urban areas using a combination of multi-regression, GIS techniques, and diffusive sampling campaigns, is an alternative to deterministic models. It can be used to achieve high spatial resolution pattern of the pollutants distribution and estimate the population exposure (Briggs et al, 2000 and Kanaroglou et al, 2005). The influence of nearby influence factors (such as population density, topography, land use, type of road, traffic volumes or emissions), is incorporated in these models at several distances by using GIS techniques, such as spatial buffering and data extraction for the monitoring locations.

This kind of statistical air quality models can be used to evaluate the new inventory model and to verify the suitability of the results as a tool to ameliorate the detail at which air quality is monitored and to support decision-making in air quality management. To demonstrate the potential of this approach in this paper will be presented the case study of the Lisbon City, making use of extensive diffusive sampling NO_2 campaigns performed in the Lisbon city, in 2001 and 2002 (Ferreira et al, 2003), and the disaggregated inventory for road and area NO_2 emissions, also for 2001 and 2002.

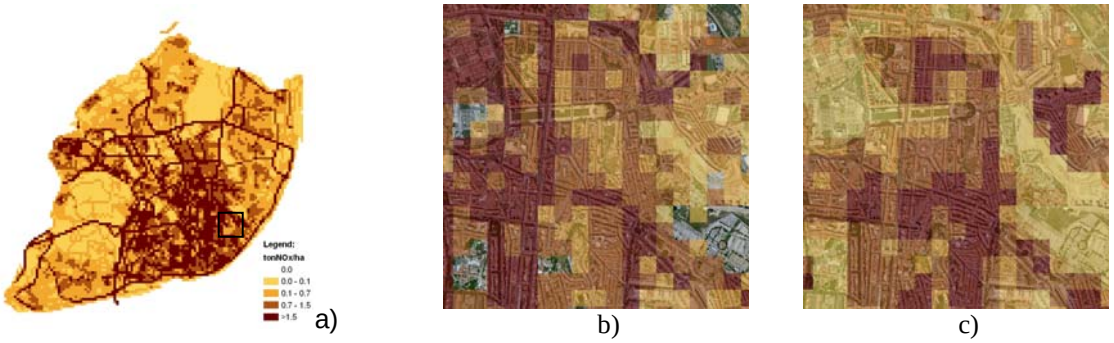
2. METHODOLOGY

Emissions from road traffic were estimated at a very detailed level using aerial photographic data - to quantify traffic volumes (q_i) - and vehicle average velocity per road link (u_i), from an on-line GPS monitoring (Gois et al, 2005). Fuel sales and commuting fluxes were used as a top-down adjustment which guarantees that estimated total kilometres (vkm^2_i) driven in Lisbon, according to the per cent of use of each fuel type (F_{flf}), match those resulting from the total consumption of fuel in the same period (TFC_f). Traffic volumes, identified for a specific period in time - hourly traffic - were extrapolated to daily average traffic (t_{FAC}) volume using data from the traffic monitoring stations operated by Lisbon municipality.

Average weighted emission factors and fuel consumption factors (FC_{ufi}), function of link velocity and the fraction of each vehicle type following the EMEP/CORINAR (EEA,2002) methodology, were adjusted to the fleet composition of the region which was obtained from field surveys made recently (Torres et al, 2006).

$$vkm_i^2 = q_i^1 \times ll_i \times \sum_f \left[\frac{TFC_f}{\sum_i \left(365 \times t_{FAC} \times F_{lf} \times FC_{ufi} \times q_i^1 \times ll_i \times 10^{-6}\right)} \right] \quad \text{, where } q_i = \frac{u_i}{k_i}$$

Non road traffic emissions were estimated using fuel sales as activity data. Emissions were disaggregated for each statistical section (average area of 9.6 ha) considering total resident population as an indicator. Air emissions were estimated for NO_x, SO_x, TSP and NMVOC in metric tonnes per year. The resultant spatial allocation of NO_x emissions is presented in Figure 1.



a) b) c)

Figure 1. NOx emissions in Lisbon area a), zoom of an area showing the road b) and area c) emissions

Two extensive campaigns were performed in the summer 2001 and the winter 2002 to evaluate air quality spatial distribution in the Lisbon region, under two different meteorological conditions, in order to complement the automated continuous measurements. In each campaign, passive diffusive samplers measuring pollutants, such as nitrogen dioxide, were exposed during a one-week period. Around 100 sampling points (Figure 2) were located in the city of Lisbon classified according to a traffic level criterion as background, intermediate, and hot spot. The nine existing fixed monitoring stations were used for quality assurance and quality control (QAQC) purposes. The QAQC proceedings allowed the estimation of the precision of the monitoring method. The method precision associated with the 1st and 2nd campaigns was 6% and 8%, respectively. The uncertainty was 47% for the summer campaign and 28% for the winter campaign.

To build the multi-regression models, basic statistics (average, minimum, maximum, standard deviation, sum and count) characterizing the road and area emissions (converted to a 10 meter grid) in the vicinity (50 meters, 50-100m, 100-250m and 250-500m) of each monitoring point (has shown on Figure 2) were calculated in ArcGIS 9.0 using Buffering tools and Zonal Statistics from Hawth's Analysis tools extension. These statistics were introduced in SPSS 12.0 to model the NO_2 concentrations, obtained from passive sampling and extrapolated to the 2001-2002 average, using multi-linear regression forward and backward stepwise options with a 0.05 significance level criteria. To obtain the spatial pattern, a grid of 100m was built. For each point the same statistics as for the campaign points were calculated and the model was applied. To validate the models, the fixed station's results were then removed from the input data.

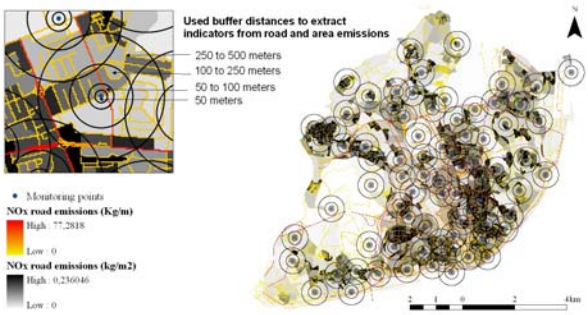
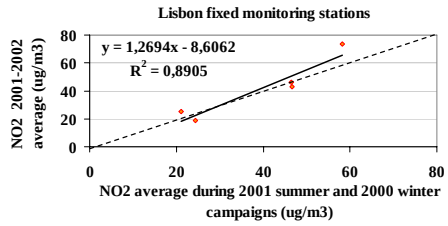


Figure 2. Rings of influence used to extract the statistics for area and road emissions inventory (10 meters grid) at several distances from the monitoring locations

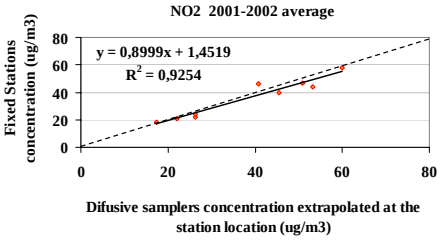
3. RESULTS AND DISCUSSION

A global average concentration for each of the 100 monitoring locations for the 2001-2002 period was calculated using the linear regression expressed in Figure 3-a), which relates the average results of the fixed stations during the periods of the campaigns and the 2001-2002 average at the same stations. The variation explained by the model was 89%. This value shows that, although the time extent of campaigns was very short, the results have a very good correlation with the annual averages. The linear regression between the diffusive samplers placed in the monitoring stations (extrapolated using the linear regression in Figure 3-a)), and the concentration averages measured at these stations by reference method monitoring equipments (Figure 3-b) has a coefficient of determination of 0.93. This indicates that, in spite of the relative high uncertainty of the campaigns, it was possible to estimate the annual averages at the measuring points with an acceptable confidence. The spatial distribution in Figure 3-c) was obtained with the geostatistical interpolation method ordinary kriging. The map shows that higher concentrations were measured at higher intensity traffic locations.

a)



b)



c)

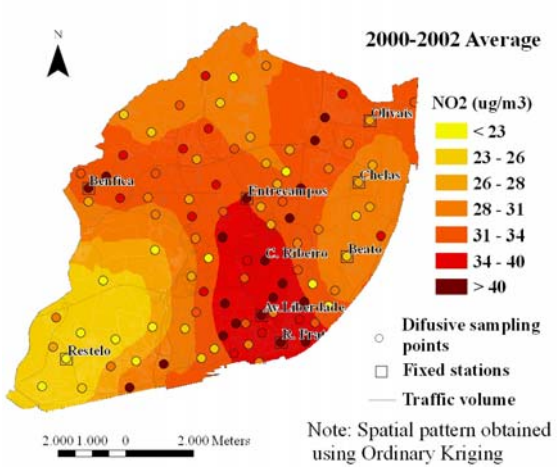
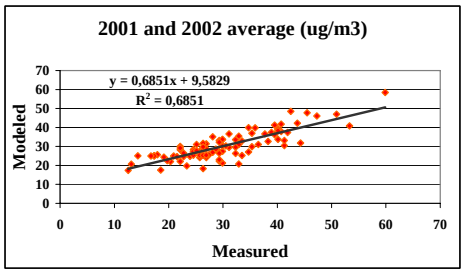


Figure 3. a) Linear regression between 2001-2002 NO_2 average concentrations and the NO_2 average results measured at fixed monitoring stations during the period of the campaigns. b) Linear regression between the fixed station's 2001-2002 average concentrations and the 2001-2002 NO_2 averages at the station's locations using the diffusive sampling results extrapolated using the linear regression from a). c) Diffusive sampling campaigns results extrapolated using a) and b) and interpolated using ordinary kriging.

Several multi-regression models were built with area and road emissions statistics, both separately and together, and for rings with different diameters, using a 0.05 significance criteria for the selection of independent variables. As expected, models integrating road emissions parameters accomplish a better explanation of the nitrogen dioxide concentration's pattern (about 50%) than area emissions (about 10%). The use of all the distance interval rings (between 0-500m), and both emission types enabled to obtain the best explanatory model. The best fitted model and its statistics, as well as the model application to a 100meters grid are shown in Figure 4. The model

coefficient of determination (R Square), shows that more than 60% of the variation in space is explained by the model.



R	0,83
R Square	0,69
Adjusted R Square	0,63
Std. Error of the Estimate	5,45

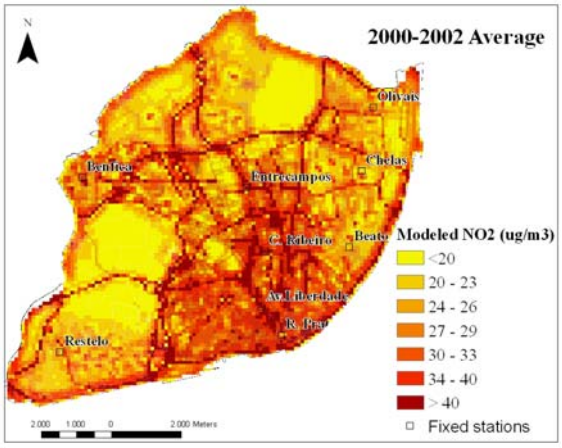


Figure 4. Best fitted NO_2 model including road and area emissions influence at several distances.

4. CONCLUSIONS

The combination of multi-regression models and GIS tools provides a suitable way to obtain, from extensive monitoring campaigns and factors influencing air quality, high resolution air quality annual maps within urban areas. This paper presents a methodology that successfully evaluates the spatially disaggregated NO_x area and road emissions inventory for the city of Lisbon relating them with the 2001-2002 NO_2 average concentrations extrapolated at 100 locations extrapolated from a two one-week passive sampler's monitoring campaigns and eight monitoring stations. NO_2 2001-2002 average concentrations can be explained by a model based on the area and road emissions desegregation at several influence ring distances. This inventory model explains more than 60% of the spatial variability of the nitrogen dioxide concentrations within the Lisbon area. It was also shown that this inventory desegregation can be used to model and map Lisbon traffic related air quality, with an acceptable error. This work should be considered as a first application of this methodology. In the future, this type of approach will be applied to evaluate other traffic related pollutants and other emission inventory spatial allocation models.

5. REFERENCES

Briggs, D., de Hoogh, C., Gulliver, J., Wills, J., Elliott, P., Kingham, S., et al., 2000. A regression-based method for mapping traffic-related air pollution: application and testing in four contrasting urban environments. Science of the Total Environment 253, 151–167.

EEA (2002). EMEP/CORINAIR Emission Inventory Guidebook - 3rd ed. Update Technical report No 30, Environment European Agency (http://reports.eea.europa.eu/EMEPCORINAIR4)

Ferreira, F., Nogueira, L., Meireles, P., Mesquita, S., Almeida, C., Tente, H. Torres, P .2003. Integrating diffusive sampling and monitoring stations to evaluate air quality in urban areas, in UAQ4 Conference, 25-28 March 2003, Charles University Prague, Czech Republic.

Gois, V., Nogueira, L., Almeida, C., Maciel, H., Torres, P. (2005). Using aerial photographic data for inventory of air emissions from road traffic sources: case study in the city of Lisbon. WIT Transactions on Ecology and the Environment, Vol. 82, ISSN 1743-3541 (on-line), pp. 337-347. (http://library.witpress.com)

Gois, V., Torres, P., Nogueira, L., Maciel, H. e C. Almeida (2006). Inventário de Emissões Atmosféricas na Região de Lisboa e Vale do Tejo 2000-2001. Inventar e CCDR-LVT, Lisboa. (http://www.ccdr-lvt.pt)

Kanaroglou, P. S. Jerrett, M. Morrison, J. Beckerman, B. Arain, M. A. Gilbert, N. L. Brook, J. R. 2005 Establishing an air pollution monitoring network for intraurban population exposure assessment: A location-allocation approach. Atmospheric Environment 39 (2005) 2399–2409

Torres, P., Gois, V., Maciel, H., Nogueira, L., Almeida, C. (2006). Caracterização da frota automóvel nos concelhos de Cascais, Oeiras e Lisboa. Comissão de Coordenação e Desenvolvimento Regional de Lisboa e Vale do Tejo.

THE INFLUENCE OF GEAR CHANGE ON VEHICLE EXHAUST EMISSIONS. CALCULATIONS WITH THE VETESS EMISSION TOOL

[1,2]Beckx, C., [1]Int Panis, L., [2]Janssens, D., [1]De Vlieger, I.. and [2]Wets, G.
[1]Flemish Institute of Technological Research,
Boeretang 200, 2400 Mol - Belgium
[2]Transportation Research Institute - Hasselt University
Wetenschapspark 5/6, 3590 Diepenbeek - Belgium
corresponding author: carolien.beckx@vito.be +32(0)14 33 59 58

ABSTRACT
This study explores the influence of gear changing behaviour on vehicular exhaust emissions and fuel consumption using the emission simulation tool VeTESS (Vehicle Transient Emissions Simulation Software). VeTESS was used to assess the impact of (not) changing gear at certain vehicle speeds on the exhaust of vehicle air pollutants using theoretical drive cycles as input. The hypothesis formulated is that, by selecting a higher gear early, one will avoid high engine speeds and achieve a reduction of emissions and fuel consumption. Calculations to test this hypothesis were executed for two vehicles of the Belgian fleet: a Euro III diesel car and a EURO IV petrol car. The results for CO_2, CO and HC confirm the hypothesis and show that one can save fuel and decrease vehicle exhaust emissions by changing up gear. The results for NO_x and PM, on the other hand, differ slightly.

1. INTRODUCTION
Large reductions in vehicle emissions can be achieved by improvements in vehicle technology. These enhancements have a relatively large implementation time and considerable costs. Furthermore, these measures are often regulated at a high policy level, limiting the contribution of the local authorities to this regard. On the other hand, policy measures to improve fuel economy can also be taken at a lower policy level, like actions focusing on a change in driver behaviour to promote environmentally friendly driving (De Vlieger et al, 2000). An environmentally friendly driving style includes different behavioural aspects to obtain a more fuel-efficient driving, one of them implying a selective use of gears (Beckx et al, 2006). By shifting gear early one can avoid high engine speeds and therefore achieve a reduction of emissions and fuel consumption. Before implementing aiming this kind of measures, it is important to assess the potential benefits of these actions in advance.
This paper presents the methodology that was used to assess the impact of an improved gear change behaviour on vehicle exhaust. It will present the results of calculations that were made for gear changes with two different vehicle types, using the VeTESS emission model. Finally, the paper concludes and defines some interesting topics for further research.

2. METHODOLOGY
The methodology to calculate the emissions from vehicles driving at a certain speed in a certain gear consists of the two important steps:

- development of speed profiles, including information on gear selection
- calculation of emissions with the VeTESS emission tool

This procedure was suggested by the head of the team that originally developed VeTESS (De Bal, 2006 pers. comm.). In this section, we discuss these steps in more detail.

To estimate the impact of (not) changing gear at a certain vehicle speed, theoretical driving cycles were developed for two different vehicle types, a Euro III diesel car (Scoda Octavia) and a EURO IV petrol car (Volkswagen Polo). We believe these vehicles are representative for an important fraction of current passenger car sales in Belgium. First, for each vehicle type, the range of speeds that can be driven at a certain gear was defined, taking into account the minimum and maximum engine revolutions per minute (RPM) of the vehicle. Next, speed profiles were developed consisting of second-by-second vehicle speed data and information on gear selection. The first speed profile started with the lowest possible vehicle speed (taking into account the minimum engine RPM) in first gear. Every 30 seconds vehicle speed was raised with 2 kph, until the maximum engine RPM was reached. Next, this procedure was repeated for the range of speeds that can be driven in second gear, third gear, etc. As a result, for every vehicle type, 5 speed profiles were developed.

These speed profiles were used as input for the VeTESS emission model. VeTESS (VEhicle Transient Emissions Simulation Software) was developed within the EU 5th framework project DECADE (2001-2003) as a vehicle level simulation tool for the simulation of fuel consumption and emissions. The calculations in

this vehicle simulation tool are based on a detailed calculation of the engine power required to drive a given vehicle over any particular route. It calculates emissions and fuel consumption on a second-by-second basis for a specific vehicle on a given speed profile, based on the required engine power. We refer to Pelkmans et al. (2004) for a detailed technical description of the VeTESS-model. For the moment detailed engine maps are only available for a few types of vehicles. Simulations in this study were performed on a Euro III diesel car (Scoda Octavia) and a EURO IV petrol car (Volkswagen Polo), as described in Beevers and Carslaw (2005). As a result of this procedure, detailed emission estimates were available for every vehicle speed and gear choice of the two selected vehicle types.

3. RESULTS AND DISCUSSION

According to the methodology described in the previous section, calculations were performed on two different vehicle types. Following graphs each represent the emission factors for a certain pollutant in function of the vehicle speed and gear selection. The emission factor was calculated as the average emission value during a few seconds of a certain speed profile, taking into account the distance that was covered. Figure 1 presents the emission factors as a function of vehicle speed and gear selection for the EURO III diesel car Scoda Octavia. In figure 2 the emission factors for the EURO IV petrol car are presented.

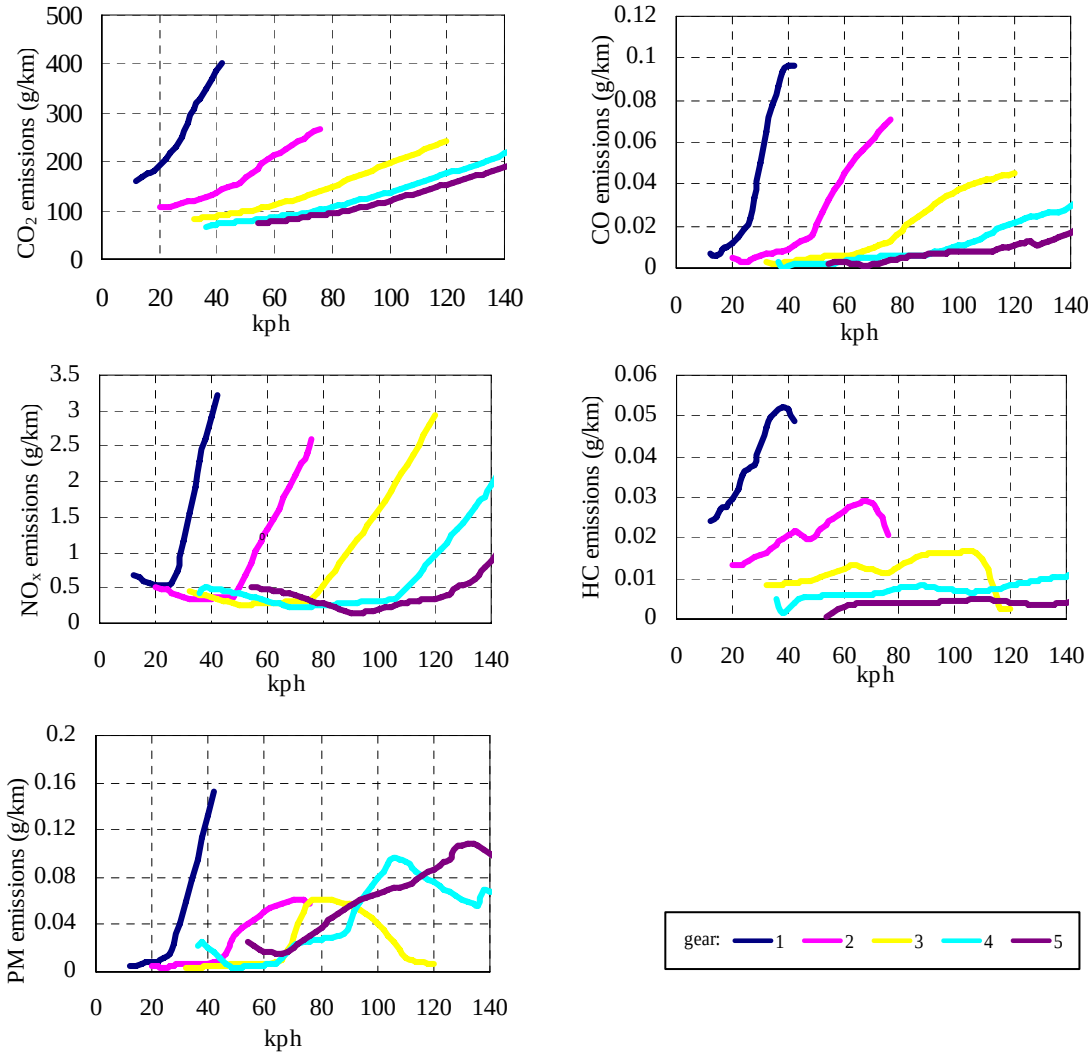


Figure 1. The emission factors as a function of vehicle speed and gear selection for the Euro III diesel car Scoda Octavia.

In figure 1 the influence of gear selection on emissions for the diesel car is clearly demonstrated for CO_2, CO and HC. When changing up gear early, the emission of these pollutants will be reduced. When driving for example 20 kph in first gear with this diesel car you will emit significantly more CO_2 than when shifting up to second gear. These findings also apply for other gear changes. For NO_x this conclusion is not straightforward since the NO_x curve seems to display a small bend in the course. The graph for PM, on the other hand, shows larger variations in the course compared to the other pollutants. Reasons for these variations are not yet clear, but difficulties in the measurements of particulate matter and the ensuing large uncertainty for PM predictions need to be examined more thoroughly before real conclusions can be drawn for this pollutant.

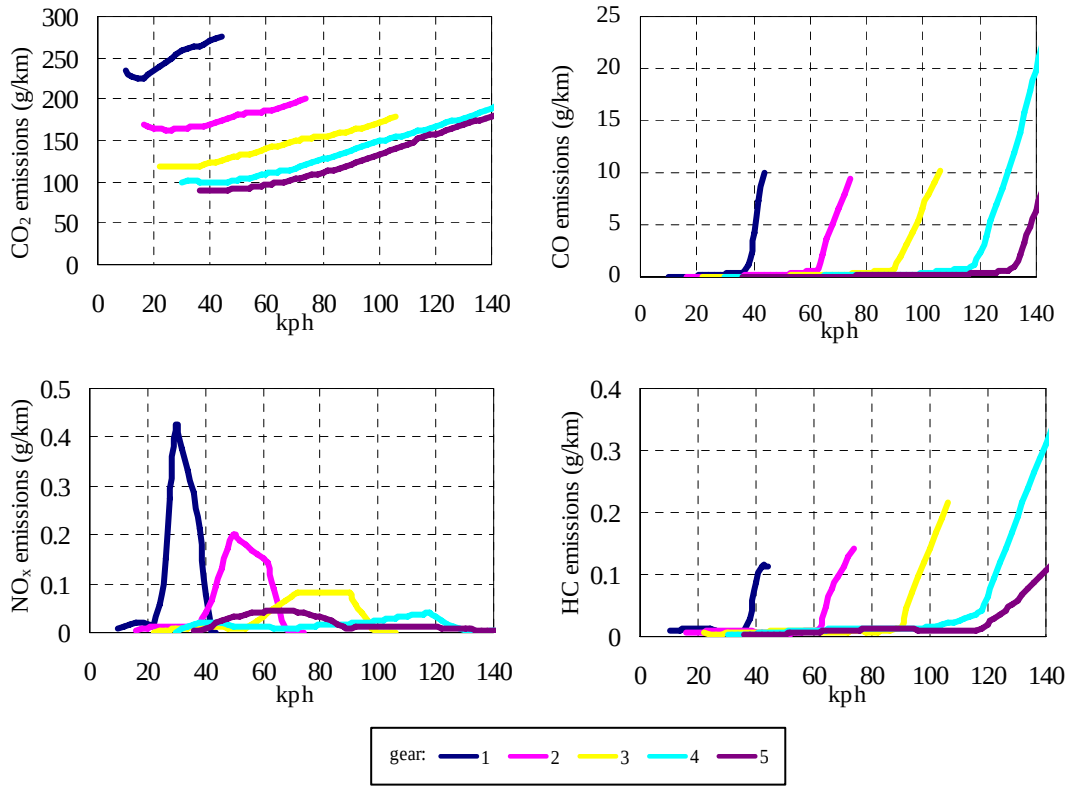


Figure 2. The emission factors as a function of vehicle speed and gear selection for the EURO IV petrol car Volkswagen Polo.

Figure 2 presents the emission results for the petrol car. Since PM emissions for petrol cars are not considered in the VeTESS model, no results are presented for this pollutant. The graph for CO_2 shows large resemblances to the CO_2 graph for the diesel car meaning that CO_2 emissions can be reduced when changing up gear early. The graph for CO resembles the one for HC, showing that driving in the 'right' gear will lead to very low emission estimates while remaining in a lower gear too long will cause a strong increase of emissions. The curves in the NO_x graph show a very different course with high NO_x peaks in first gear and lower peaks in higher gear selections.

4. CONCLUSIONS

Theoretical speed profiles were used to assess the impact of gear change on vehicle exhausts of two vehicle types by using the VeTESS emission tool. The results clearly show that both the Euro III diesel car and the EURO IV petrol car can reduce the emissions of CO_2 (and fuel consumption) when shifting up gear early. The same findings apply to CO and HC, but cannot be made for NO_x and PM. The large uncertainty ensuing from difficulties in the PM measurement can be the cause of these variations but needs to be studied thoroughly before drawing conclusions.

Since this study dealt with theoretical, non-realistic speed profiles the real impact of an improved gear changing behaviour on emissions could not be quantified. The use of real life driving cycles with information on gear choice will improve these assessments offering useful information to policy makers who aim at promoting an environmentally friendly driving behaviour. Future research should therefore include large scale monitoring programs to gain more insight into this matter. In 2007 a travel survey will be initiated in Flanders (Belgium) as a part of the research project "An activity based approach for surveying and modelling travel behaviour". The analysis of these data will hopefully provide more information on the problem of gear changing behaviour and emissions.

5. ACKNOWLEDGEMENTS

The authors wish to thank Luc Pelkmans and Patrick De Bal for making the VeTESS model available for this study.

6. REFERENCES

Beckx, C., Int Panis, L., De Vlieger, I. and Wets, G. 2006. Influence of gear changing behaviour on fuel-use and vehicular exhaust emissions. In: Proceedings of the 8th International Symposium on Highways and the Urban Environment. Rauch S. & Morrisson G. (eds.), Chalmers University. (in press)

Beevers, S.D. and Carslaw, D.C. 2005. The impact of congestion charging on vehicle speed and its implications for assessing vehicle emissions. Atmospheric Environment, Vol. 39, p. 6875-6884.

De Vlieger, I., De Keukeleere, D. and Kretzschmar, J.G. 2000. Environmental effects of driving behaviour and congestion related to passenger cars. Atmospheric Environment, Vol. 34, p. 4649-4655.

Pelkmans, L., Debal, P., Hood, T., Hauser, G. and Delgado, M.R. 2004. Development of a simulation tool to calculate fuel consumption and emissions of vehicles operating in dynamic conditions. In: Proceedings of the Society of Automotive Engineers International Conference, June 2004, Toulouse, France, 2004-01-1873, ISBN 0-7680-1480-8.

HEAVY METALS EMISSION INVENTORY IN THE CZECH REPUBLIC

Jitka Hlavicova[1], Ilona Dvorakova[1], Radomir Srnensky[2]
[1]Czech Hydrometeorological Institute, Prague, hlavicova@chmi.cz
[2]IDEA –ENVI s.r.o., Valasske Mezirici

ABSTRACT

During last years considerable attention was paid to emissions of heavy metals (HMs) and to the quality of their emission inventories in the Czech Republic. This is a result of both amended structure of emission inventory EMEP (Co-operative programme for monitoring and evaluation of the long range transmission for air pollutants in Europe) and harmonization of Czech emission inventories with EU. HMs emissions are observed and inventoried from the base year 1990 till present and the result are reported in required format to the secretariat of United Nations Economic for Europe (UNECE) to Geneva annually.

1. INTRODUCTION

Czech Hydrometeorological Institute (CHMI) is authorized organization by the Ministry of Environment of the Czech Republic for processing emission inventories of air pollutants including heavy metals emissions as well. CHMI is also authorized for preparing of reporting for UNECE secretariat in Geneva on the basis of international conventions which are obligatory for the Czech Republic.

According to the Protocol on Heavy Metals concluded in year 1998 to the Convention on Long-Range Transboundary Air Pollution (CLRTAP) the emissions of Cd, Hg and Pb are included in the obligatory reporting. As it was mentioned the Czech Republic provides these emissions from 1990 and begun to provide other metals emissions (As, Cr, Cu, Ni, Se, Zn) from 2001. This was a result of amended structure of emission inventory EMEP (Co-operative programme for monitoring and evaluation of the long range transmission for air pollutants in Europe). Last year we made additional calculation for other six metals emissions because of refilling time series from 1990 to 2000.

2. METHODOLOGY

Heavy metals emission inventory is presented in this paper. We produce it mainly with using relevant capacity data (fuel and propellant consumption, incinerated waste quantity, statistical data on the production of selected technological processes) and emission factors. Additionally, there were included emission data provided by sources operators directly in the last years.

Following heavy metals were considered: lead (Pb), cadmium (Cd), mercury (Hg), chromium (Cr), nickel (Ni), copper (Cu), arsenic (As), selenium (Se) and zinc (Zn).

Most of above mentioned heavy metals are usually released during the combustion process as compounds (e. g. chlorides, oxides) together with the solid particles. Only Hg and Se are presented as vapors in small amount. Less volatile elements condense easily on surface of the fine particulates presented in exhaust fumes. For that reason fine particles fraction is enriched by these elements.

Amount of heavy metals emissions depends on their content in fossil fuels mainly. In the case of technological processes it depends on their content in original raw material. Additional, it is affected by physical and physically-chemical properties of individual heavy metals e.g. properties affecting production of their vapors in combustion equipment and following condensations on fine particles in the exhaust fumes (temperature in combustion equipment, volatility etc.). The technology of industrial processes or type and efficiency of abatement equipment influence final emission amount released into the air too.

Capacity data

The capacity data using for calculation of emission inventories were obtain from the database of Register of Emissions and Air Pollution Sources (REZZO). Pursuant to the legislation valid until 2002 air pollution sources were divided into four categories to carry out emission inventories. Complying with this categorization, the ISKO (Air Quality Information System) system operated by CHMI includes REZZO 1-4 databases which serve for archiving and presenting data on stationary and mobile air pollution sources. Figure 1 describes the structure of REZZO database.

The data used in the emission inventory from extra large and large sources are extracted from summary operational inventory submitted by sources operators. Based on these data the REZZO 1 database is updated, and namely the constant and variable data on operation of air pollution sources (categorization of source, parameters, fuel consumption and emission quantity).

Inventories of emission from transport, falling within the competency of the Ministry of Transport, is processed by the Transport Research Centre (CDV) Brno based on the updated method of determination of transport emission.

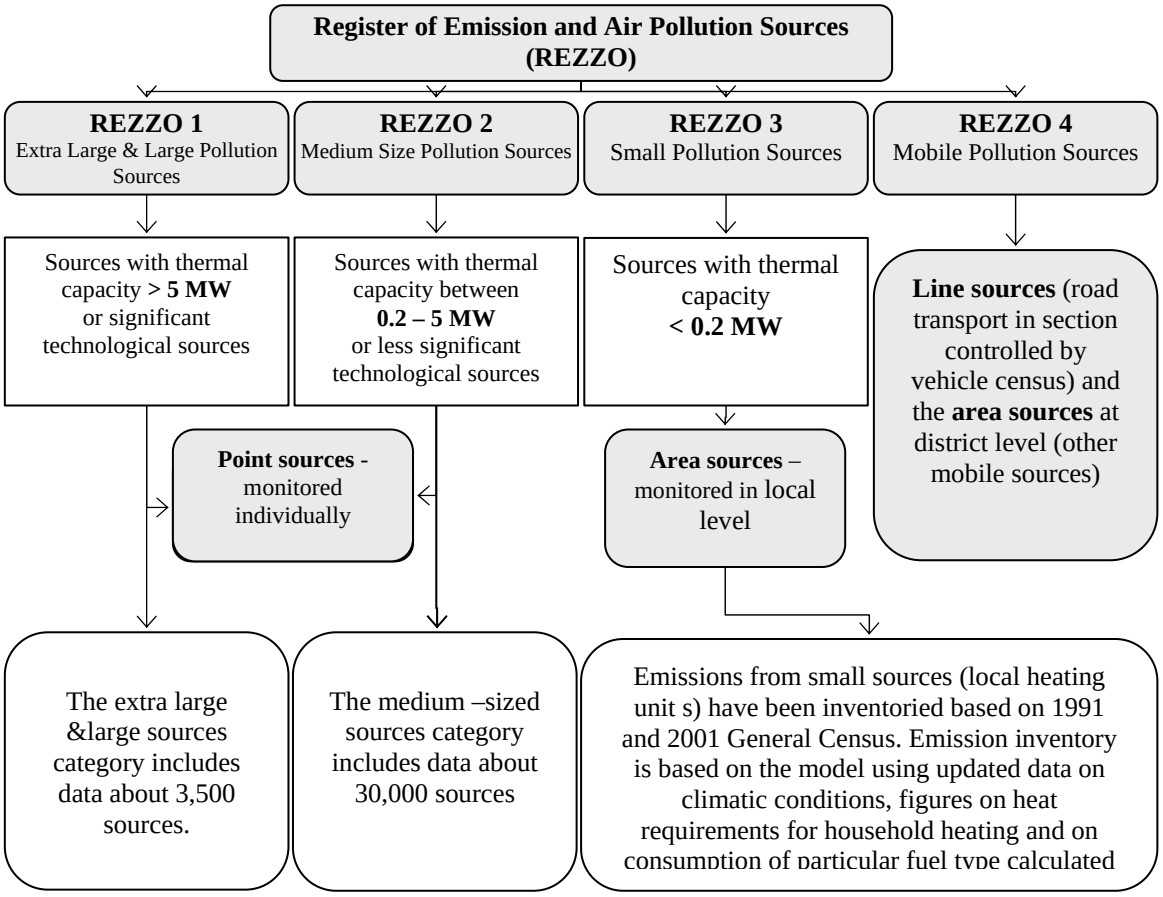


Figure 1. Register of Emission and Air Pollution Sources Structures (REZZO)

Emission factor database

The database of emission factors was corrected and refined where necessary. During setting up new database there were preferred values obtained by measuring on sources in the Czech Republic. Database of measured emission factors was compared with available information from other relevant sources. This comparison was primarily focused on emission factors measured in other countries of CEE region, especially in Poland and Slovakia, and emission factors published in Emission Inventory Guidebook. In case of missing values emission factors were adopted from the Emission Inventory Guidebook while taking into account technical level of technologies used in the Czech Republic. For mobile sources there were used emission factors which were elaborated by Transport Research Centre.

Table 1. Emission factors for selected technological processes

Technological process	NFR	Cd mg/Mg	Hg mg/Mg	Pb mg/Mg
Sinter plants	1A2a	59.00	17.00	3 373.00
Grey iron production	1A2a	4.00	36.00	163.00
Secondary aluminum production	1A2b	7.00	0.00	37.00
Cement production	1A2f	8.00	275.00	216.00
Coke oven	1B1b	10.00	10.00	250.00
Pig iron tapping	2C1	0.20	10.88	287.81
Electric furnace steel plants	2C2	173.15	0.00	731.94

3. RESULTS

The trends of selected heavy metals emissions (Cd, Hg and Pb) in 1990 – 2004 are given in Figures 2-4. Cd, Hg and Pb emissions have stable decreasing tendency from 1990. The significant decrease in the emissions of Pb was caused by the gradual decrease and, from January 1, 2001, the complete termination of the sales of leaded automotive petrol.

Power generation and heating, ferrous and non ferrous metal production, waste incineration, production of mineral product (cement production in the case of Hg) and transport (in the case of Pb) belong among sectors which contribute to the total emission these heavy metals significantly.

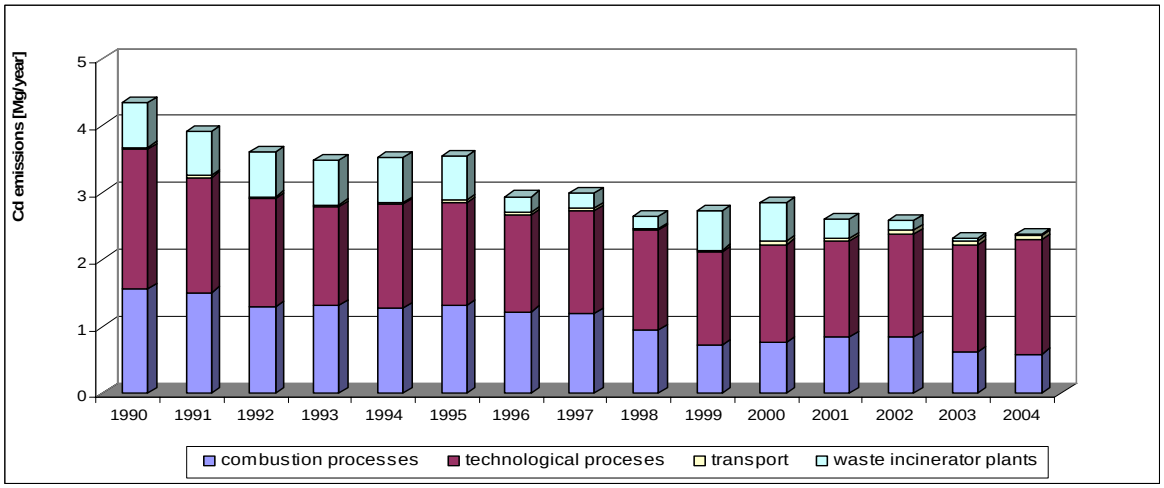


Figure2. Cd emission trend in the Czech Republic in 1990 - 2004

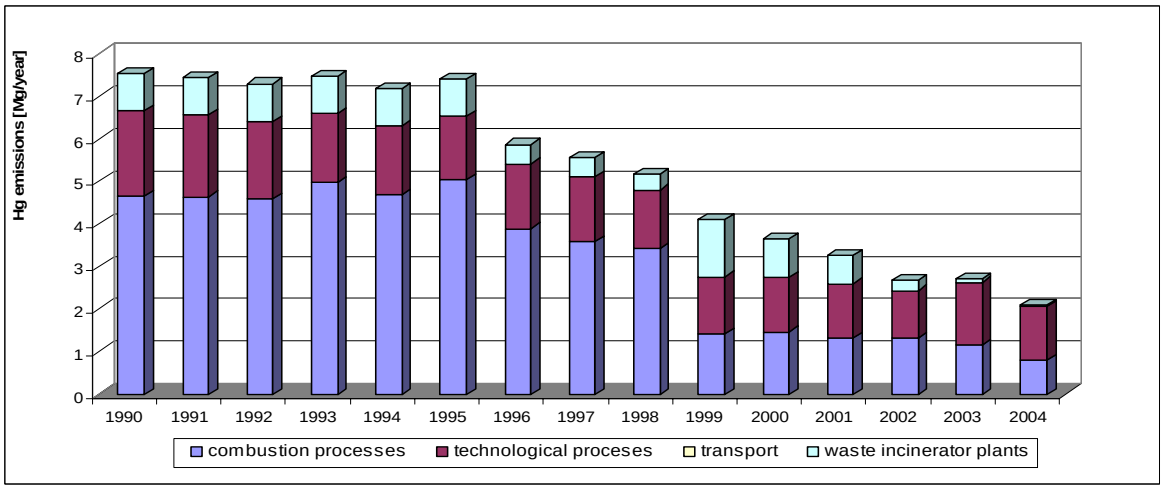


Figure3. Hg emission trend in the Czech Republic in 1990 - 2004

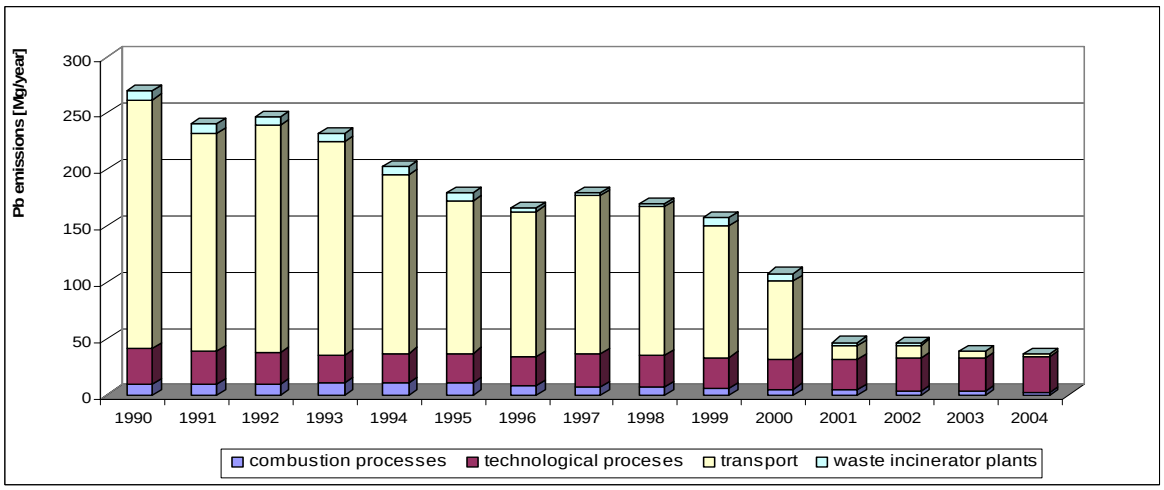


Figure4. Pb emission trend in the Czech Republic in 1990 - 2004

Emission data processed into charts with the help of GIS are shown in following Figures 5. Emission densities for Cd and Hg are plotted in 5x5-km grid-squares. The charts are based on current emissions from stationary sources (REZZO 1-3) and mobile sources (REZZO 4) for 2004, with regional disaggregation of emissions from line sources according to the 2000 vehicle census.

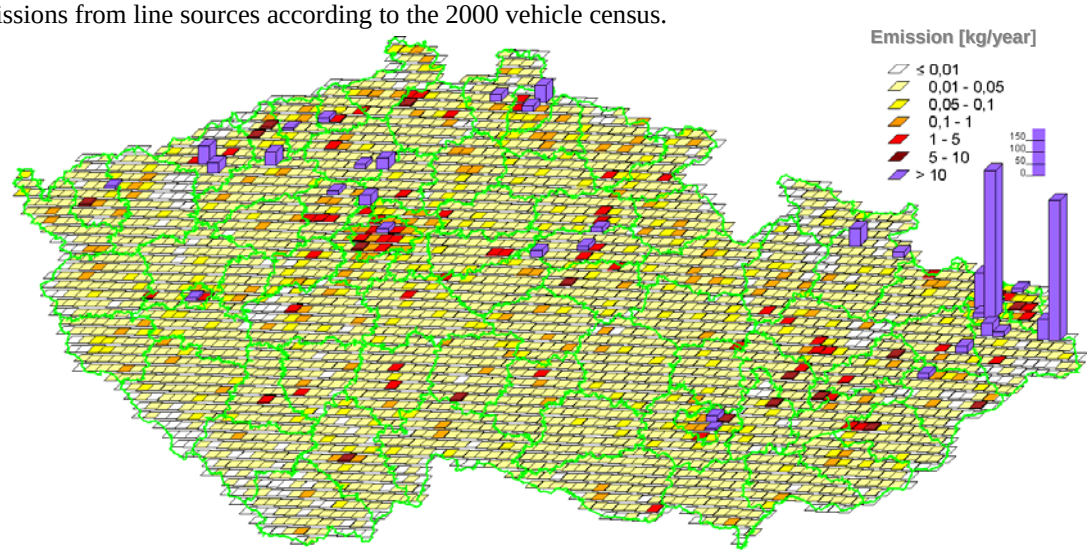


Figure 5. Cd emission density from 5x5 km squares, 2003

4. CONCLUSIONS

The emission trends of selected heavy metals from 1990 to 2004 introduced in Figures 2-3 have decreasing tendency. The significant decrease in emissions from 1990–1995 was caused particularly by enormous investment to desulphurization of power plants and by changes in national economy (production decrease and restructuring), and from 1996 to 1999 also by the partially subsidised overall replacement of fuels (small and medium sources) and the fulfillment of the legislative requirements related with the general validity of emission limits provided by Decree 117/1997 of the Ministry of the Environment.

There was a decreasing tendency in the volumes of emissions during almost the entire period in question, caused by changes in the composition of vehicles on the roads (an increasing share of cars with catalysers), while on the other hand, the actual volumes of emissions increased owing to the dynamic growth in transport operations, particularly as regards road transport. Other measurement that caused significant decrease of Pb emission in 2001 was termination of the sales of leaded petrol

All these above mentioned measurements contributed to the reduction of heavy metals emissions from the based year 1990 to 2004 by 72 % for Hg, 86 % for Pb and 45% for Cd.

5. REFERENCES

EMEP/CORINAIR, 2006,Atmospheric Emission Inventory Guidebook, 3rd edition.
http://reports.eea.europa.eu/EMEPCORINAIR4/en/page002.html

Labounek P. and editorial team. 2005. Report on the Environment in the Czech Republic in 2004, Ministry of the Environment. Prague.

Olendrzynski K., Fudala J., Hlawiczka S., Cenowski S., Kachniarz M., Kargulewicz I., Debski B. Skoskiewicz J. 2002. Emission Inventory of SO2, NO2, NH3, CO, PM, HMs, NMVOCs and POPs in Poland 2000; UN-ECE – EMEP/Poland – Report/2002; IOS, Warszawa.

Ostatnicka, J. Editor, 2006. Air Pollution in the Czech Republic in 2005. Czech Hydrometeorological Institute, Air Quality Protection Division. Prague

EMISSION INVENTORY OF CARBON MONOXIDE AND NITROGEN OXIDES FOR AREA SOURCES AT BUENOS AIRES METROPOLITAN AREA (ARGENTINA)

A. L. Pineda Rojas, L. E. Venegas and N. A. Mazzeo
National Scientific and Technological Research Council (CONICET).
Department of Atmospheric and Oceanic Sciences. Faculty of Sciences. University of Buenos Aires.
Ciudad Universitaria. Pab. 2. 1428-Buenos Aires. Argentina.
pineda@at.fcen.uba.ar - venegas@at.fcen.uba.ar - mazzeo@at.fcen.uba.ar

ABSTRACT

The results of an emission inventory of CO and NO_x for the Buenos Aires Metropolitan Area (BAMA) are presented. The inventory includes area source emissions: residential, commercial, small industries, road traffic and aircrafts landing/take-off at both the domestic and the international airports. The inventory has a spatial resolution of 1 x 1 km. The emission factors used are based on measurements of in-service emissions in Buenos Aires and on the recommended by US. Environmental Protection Agency and the European Enviroment Agency. These factors were applied to fuel consumption, gas supply data and vehicle kilometres travelled within each grid square. Data on traffic flow and bus service frequencies were also available. We obtained spatial and time dependent area source emission distributions in the BAMA. Annually, 99.4% of CO and 80.6% of NO_x area source emissions within the BAMA can be allocated to road transportations.

1. INTRODUCTION

An air pollution emissions inventory is a schedule of the sources of an air pollutant or pollutants within a particular geographical area. An emission inventory usually includes information on the amount of the pollutants released from major industrial sources, and average figures for the emissions from smaller sources throughout the area. Emission inventories are an essential tool in the management of local air quality: identify the sources and help in the development of abatement strategies.

Air pollution emission inventories have been developed for several urban areas (Sallés et al., 1996; Mensink, 2000; Saija and Romano, 2002; Aleksamdropoulou and Lazaridis, 2004; Ariztegui et al., 2004; Miller et al. 2006; Parrish, 2006). Particularly, five years ago, an urban emission inventory (year 2000) has been prepared for the city of Buenos Aires (Mazzeo and Venegas, 2003).

This paper summarises the results of the first version of an emission inventory of carbon monoxide (CO) and nitrogen oxides (NO_x) for the Metropolitan Area of Buenos Aires which includes area source emissions (motor vehicles, aircrafts, residences, commercial and small industries). The inventory also includes an update of area source emissions in Buenos Aires city. Annual emissions of CO and NO_x from each area source category are summarised. The spatial distributions of CO and NO_x annual emission rates from area sources within the Buenos Aires Metropolitan Area are shown with a resolution of 1 x 1 km.

2. METHODOLOGY

The Buenos Aires Metropolitan Area (BAMA) is integrated by the city of Buenos Aires (CBA) and the Greater Buenos Aires (GBA). Buenos Aires city (Lat. 34°35'S – Long. 58°26'W), capital of Argentina, is located on the west coast of the de la Plata River. The city has an extension of 203km^2 and 2776138 inhabitants. Buenos Aires city is surrounded by the Greater Buenos Aires. This area is compound by 24 districts. It has an extension of 3627km^2 and 8684437 inhabitants. The BAMA is considered the third mega-city in Latin America, following Mexico (Mexico) and Sao Paulo (Brazil).

The annual mean temperature in the city of Buenos Aires is 18°C, and it ranges between 15-16°C in the Greater Buenos Aires.

In the BAMA there are usually more than three million vehicles circulating during working days. The inventory includes the CO and NO_x emissions from the following major area sources: domestic, commercial, small industries, road transport (buses, cars, trucks) and aircrafts. Point source emissions have not been considered because, at present, there is not available sufficient data on the large industries located in the Greater Buenos Aires. Information on the actual point source emissions is only available in a limited number of cases.

It is impossible to measure every emission source in an urban area with a population of several million in order to prepare an emissions inventory. Therefore, the majority of emissions has to be estimated from other information such as gas or fuel consumptions, vehicle kilometres travelled or some other measure of activity relating to the emissions. For the pollutants of concern, the major source of emissions is combustion of fossil fuels. Consequently, the collection and analysis of the consumption statistics plays an important part in the preparation of emission inventories. However, it is important to consider the differences between consumption and fuel deliveries when making use of the available data. Most of the readily statistics relate to fuel deliveries which, in many cases, relate closely to consumption. However, in the case of fuels which may be stockpiled, there may be significant differences between delivery and consumption. Emissions factors are then applied to the activity data in order to estimate the likely emissions: activity rate x emission factor = emission.

In this study, the emission factors used in preparing the emissions inventory were derived considering: a) monitoring studies undertaken in Buenos Aires (Rideout et al. 2005); b) The EMEP/CORINAIR Atmospheric Inventory Guidebook (European Environment Agency, 2001); c) The US Environmental Protection Agency's manual on the Compilation of Air Pollution Emission Factors (US.EPA, 1995).

We divided the whole BAMA into a grid net with a resolution of 1 x 1 km. The small size fixed sources as domestic, commercial and small industries were considered as area sources. These activities use natural gas as fuel consumption. Using the natural gas consumed by these activities in the BAMA, the spatial distribution of population density, the land use maps and the corresponding emission factors for CO and NO_x, emission rates of these source categories were estimated at each grid cell.

The CO and NO_x emissions from buses were computed from the total distance travelled by each passenger car within each grid cell, the bus services frequency and the mean velocity of the vehicles in the grid cell. The emission rates of CO and NO_x from other motor vehicles (car/taxis and trucks) were estimated using historical car volume data. The National Secretary of Transportation, the Buenos Aires City Government and the Secretary of Transportation of the Province of Buenos Aires carry out traffic flow observations at different highways, roads, avenues and main streets within the BAMA. The frequency of these observations may vary from almost continuously to as infrequently as some observations at several points of the area during a few days. Depending on the available amount of vehicle speed and traffic flow data in each grid cell, temporal and spatial extrapolations were needed. The extrapolations were based mostly on empirical assumptions. Vehicle rates (R) were extrapolated anywhere along every road in the BAMA. As measurements were not numerous enough along every road, assumptions were made in order to extrapolate these values. In the GBA highways, roads, avenues and main streets can clearly be grouped into radial and semi-circular roads. According with available data, radial road rates continuously decreased with the distance (X) to the border of the city of Buenos Aires. Semi-circular road rates do not vary in space within different sectors. An empirical exponential law (Sallés et al, 1996) was chosen to describe this typical star-form network behaviour: $R=R_0 \exp[-\alpha X]$, with R_0 a reference value (traffic flow at the border of the CBA) and α an empirical coefficient. The values of α were obtained by fitting to traffic flow measurements registered at several points in different highways and roads. It is difficult to define a law for spatial vehicle speed evolution along a road. In this study the vehicle speed was set as a function of road type (highway, road, avenue, main street, secondary roads) and vehicle class (car passengers, light duty vehicles, buses, coaches, trucks). The emission factors used for mobile sources were derived from the measurements of in-service vehicle emissions, undertaken in Buenos Aires (Rideout et al. 2005). The vehicle emission rates were computed considering a daily cycle of flow traffic, the vehicle kilometres travelled within each grid square and the emission factors.

There is a domestic airport (Buenos Aires Airport) on the banks of the de la Plata River in the northern part of the CBA and an international airport (Ezeiza Airport) located in the GBA, approximately 25 km southwest away from the city of Buenos Aires. Aircraft emissions were computed knowing the scheduled hourly flights, the type of aircraft, the information available on LTO (landing/take-off) cycles and CO and NO_x emission factors (Romano et al, 1999, EMEP/CORINAIR, 2001). The aircraft emissions were added to the area source emissions estimated for the grid cells where the airports were located.

3. RESULTS

The CO and NO_x annual area source emission rates estimated for the City of Buenos Aires (CBA), the Greater Buenos Aires (GBA) and the Buenos Aires Metropolitan Area (BAMA) are included in Table 1.

Table 1. Estimated annual emissions of CO and NO_x for area sources in CBA, GBA and BAMA

Pollutant	City of Buenos Aires (CBA)	Greater Buenos Aires (GBA)	Buenos Aires Metropolitan Area (BAMA)
CO	324.7 Gg $year^{-1}$	294.6 Gg $year^{-1}$	619.3 Gg $year^{-1}$
NO_x	22.9 Gg $year^{-1}$	43.9 Gg $year^{-1}$	66.8 Gg $year^{-1}$

The intensity of area source emissions varies considerably across the Buenos Aires Metropolitan Area depending on the sources. This variation can be seen in Figures 1 and 2. These Figures show the spatial distribution of annual emissions of CO (Figure 1) and NO_x (Figure 2) from road traffic, residential, commercial, small factories and aircrafts operating in the domestic and international airports. They clearly show the lines of the highways and main roads in the area of the Greater Buenos Aires as well as the high concentration of traffic within the city of Buenos Aires.

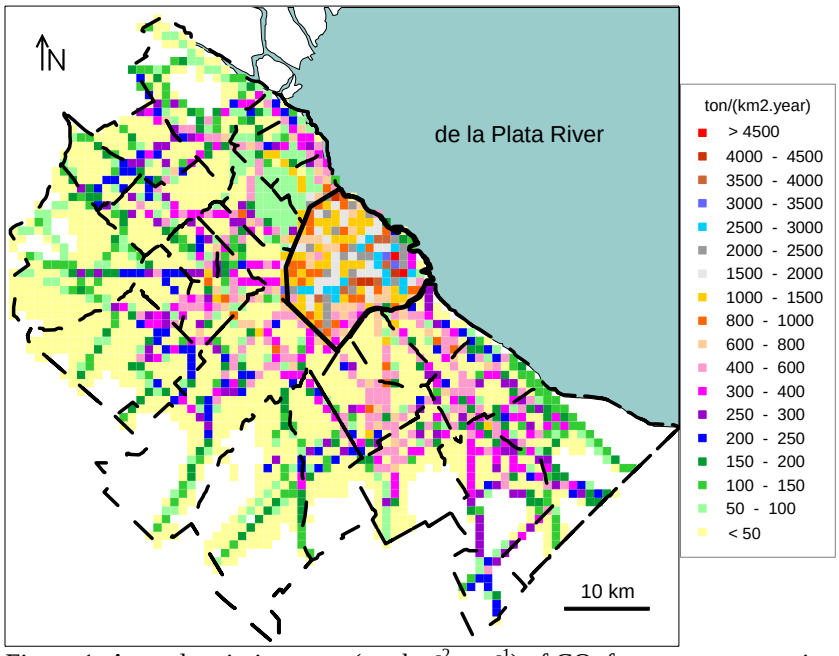


Figure 1. Annual emission rates (ton $km^{-2}year^{-1}$) of CO, from area sources in the BAMA. Grid resolution 1 x 1 km.

The Figures 3 and 4 show in diagrammatic form the distribution of annual emission of CO and NO_x by source category, for the Buenos Aires Metropolitan Area. The single most significant area source of CO and NO_x in the BAMA is road traffic (mainly associated with petrol vehicles). In the case of CO, road traffic accounts for 99.4% of annual emissions. This is because this pollutant is particularly associated with petrol-fuelled combustion engines, used in cars, and has few other significant sources. Road traffic also accounts for 80.6% of annual area source emissions of NO_x.

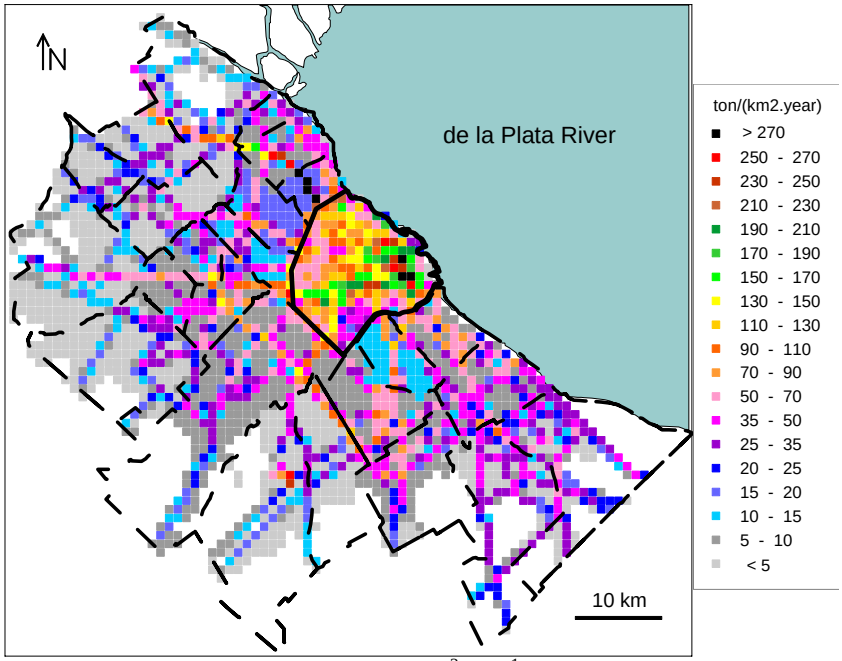


Figure 2. Annual emission rates (ton $km^{-2}year^{-1}$) of NO_x, from area sources in the BAMA. Grid resolution 1 x 1 km.

4. CONCLUSIONS

Emission inventories are an important tool to monitor the changes in the air pollutants emissions situation and to indicate if improvement measures are effective or not. In addition, they can serve as a basis for urban air quality modelling if they complete certain requirements in terms of temporal and spatial resolutions. The main results of the first version of an emission inventory of CO and NO_x from area sources in the Buenos

Aires Metropolitan Area are presented. The inventory includes mobile sources (cars/taxis, trucks, buses and aircrafts) and fixed sources (residential, commercial and small industries). The emission inventory for Buenos Aires Metropolitan Area can be characterised by the presence of an important contribution of CO and NO_x emitted from mobile sources. Mobile sources contribute with 99.4% of CO and 80.6% of NO_x annual emissions of area sources in the BAMA. The operations at the domestic airport located in the city of Buenos Aires and at Ezeiza international airport located in the Greater Buenos Aires, approximately 25 km away from the city, are the main responsible for the emissions of CO and NO_x into the grid cells where they are situated. The spatial distributions of carbon monoxide and nitrogen oxides emissions show an appreciable variation across the Buenos Aires Metropolitan Area.

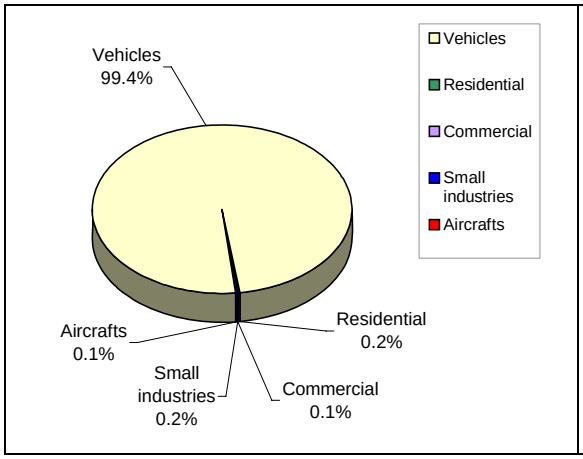


Figure 3. Estimated BAMA annual area source emissions of CO by source category.

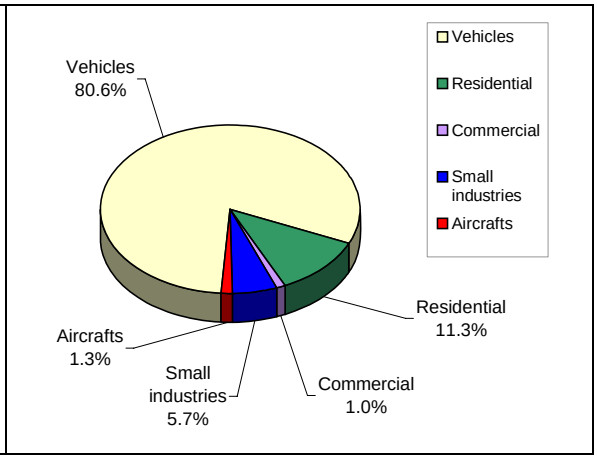


Figure 4. Estimated BAMA annual area source emissions of NO_x by source category

5. ACKNOWLEDGEMENTS

This work was supported by the Projects: UBACyT-X060 and CONICET PIP-6169. The authors kindly acknowledge support given by ENARGAS, the National Secretary of Transportation, the Buenos Aires City Government and the Secretary of Transportation of the Province of Buenos Aires on providing valuable information on fuel and gas consumptions and traffic flow patterns.

6. REFERENCES

Aleksandropoulou V. and Lazaridis M. 2004. Spatial distribution of gaseous and particulate matter emissions in Greece. Water, Air and Soil Pollution, 153, 15-34.

Ariztegui J., Casanova J. and Valdes M. 2004. A structured methodology to calculate traffic emissions inventories for city centres. Sciences of the Total Environment, 334-335, 101-109.

European Environment Agency. 2001. Joint EMEP/CORINAIR Atmospheric Emission Inventory Guidebook, Third Edition, Copenhagen.

Mazzeo N. A. and Venegas L. E. 2003. Carbon monoxide and nitrogen oxides emission inventory for Buenos Aires city (Argentina). Proceedings of the 4th International Conference on Urban Air Quality. Prague, 159-162.

Mensink, C. 2000. Validation of urban emission inventories. Environmental Monitoring and Assessment, 65, 31-39.

Miller C. A., Hidy G., Hales J., Kolb C. E., Werner A. S., Haneke B., Parrish D., Frey H. C., Rojas-Bracho L., Deslauriers M., Pennell B. and Mobley J. D. 2006. Air emission inventories in North America: a critical Assessment. Journal of the Air & Water Management Association, 56, 1115-1129.

EMEP/CORINAIR. 2001. Emission Inventory Guidebook. Air Traffic. B851.

Parrish D. D. 2006. Critical evaluation of US on-road vehicle emission inventories. Atmos. Environ. 40, 2288-2300.

Rideout G., Gourley D. and Walker J. 2005. Measurement of in-service vehicle emissions in Sao Paulo, Santiago and Buenos Aires. ARPEL Environmental Report # 25. Otawa. ESAA.Canada.

Romano D. Gaudioso D. and De Lauretis R. 1999. Aircraft emissions: a comparison of methodologies based on different data availability. Environmental Monitoring and Assessment 56, 51-74.

Saija S. and Romano D. 2002. An methodology for estimation of road transport air emissions in urban areas of Italy. Atmos. Environ. 36, 5377-5383.

Sallés, J., Janischewski, J., Jaecker-Voirol, A. and Martin, B. 1996. Mobile source emission inventory model. Application to Paris area. Atmos. Environ. 30, 1965-1975.

U.S.EPA. 1995. Compilation of Air Pollution Emission Factors, AP-42, 5th ed., United States Environmental Protection Agency, Office of Air Quality Planning and Standards, Research Triangle Park, NC.

COMPILATION OF AIR EMISSION INVENTORIES FOR WESTERN MACEDONIA, GREECE

D. Vlachogiannis[1], A. Sfetsos[1,2], N. Gounaris[1], J.G. Bartzis[2]

[1] Environmental Research Laboratory, INT-RP, NCSR Demokritos,
Patriarchou Grigoriou & Neapoleos Str., 15310, Aghia Paraskevi, Greece
Email: mandy@ipta.demokritos.gr (D. Vlachogiannis)
[2]University of Western Macedonia, Dept. of Energy Resources Engineering, Salvera & Bakola Str., 50100, Kozani, Greece

ABSTRACT

The region of Western Macedonia is a mountainous - energy intense area, producing approximately 65% of all electricity needs in Greece. A detailed study of the prevailing in the area air quality patterns and the development of a reliable real-time operational air quality modelling system demand a highly detailed air pollution emission inventory.
The developed emissions inventory includes anthropogenic and biogenic emissions emphasizing the most important ones for the region: electricity generating units (EGU), mining activities, industry, road transport and domestic heating. The inventories are characterised by seasonal variation and include the following air pollutants: NO_x, CO, SO_2, PM and VOC. The validated IMPRESSAREO (Winiwarter W., *et al.*, 2003) top-down methodology has been applied to generate emission inventories from sources such as industry, traffic, lignite mines and domestic heating. On the other hand, data from EPER has been used for EGU.

1. INTRODUCTION

The greater lignite basin of West Macedonia and FYROM is the major power supplier for Greece as well as for the neighboring country of FYROM (Fig 1). 65% of the electrical energy needs in Greece and 70% of FYROM are produced in the coal fired power plants in the region. Within the Kozani - Ptolemais basin, lignite power stations operate with a total installed generating capacity of more than 4 GW.

The epidemiological study of Papadakis et al. (2002) have shown that the crude mortality, infant mortality, as well as the specific by cause mortality in Kozani County is not basically different from that of the general Greek population. However, pollution was found to have a harmful effect on the respiratory system of children, mainly attributable to the occurrence of rhinitis and infectious bronchitis (Sichletidis, 2005)

The effect on air quality and regional climate of such an intensive anthropogenic activity needs to be systematically evaluated. Dust emissions seem to be the most serious problem in the area, as the measured ambient concentrations of suspended particles are at high levels and exceed local and international standards. A decreasing trend of TSP concentrations is reported (Triantafyllou 2000). Furthermore, studies dealing with the chemical composition and the origin of particles in the region indicated that traffic, fly ash and domestic burning as equally important pollution sources (e.g. Samara 2005). Therefore the development of a high quality emission inventory accurately portraying the main pollution sources of the area will be a valuable tool to quantify the relative impact of pollution sources in the region.

2. EMISSION INVENTORY METHODOLOGY

The inventories include the following air pollutants: NO_x, CO, SO_2, PM and VOC. The validated IMPRESSAREO (Winiwarter et al., 2003) top-down methodology has been applied to generate emission inventories from sources such as traffic, mining and domestic heating. The industrial activity in the area other than EGU was not an important factor but however, further analysis is needed in order to properly assess its full extend.
The domain covers the four prefects of Western Macedonia (Kozani, Kastoria, Grevena and Florina) with a total area of approximately 9500 km^2. The working domain was split into 72 * 72 cells of 4 km^2 each. The region is a sparsely populated area of nearly 300,000 inhabitants.

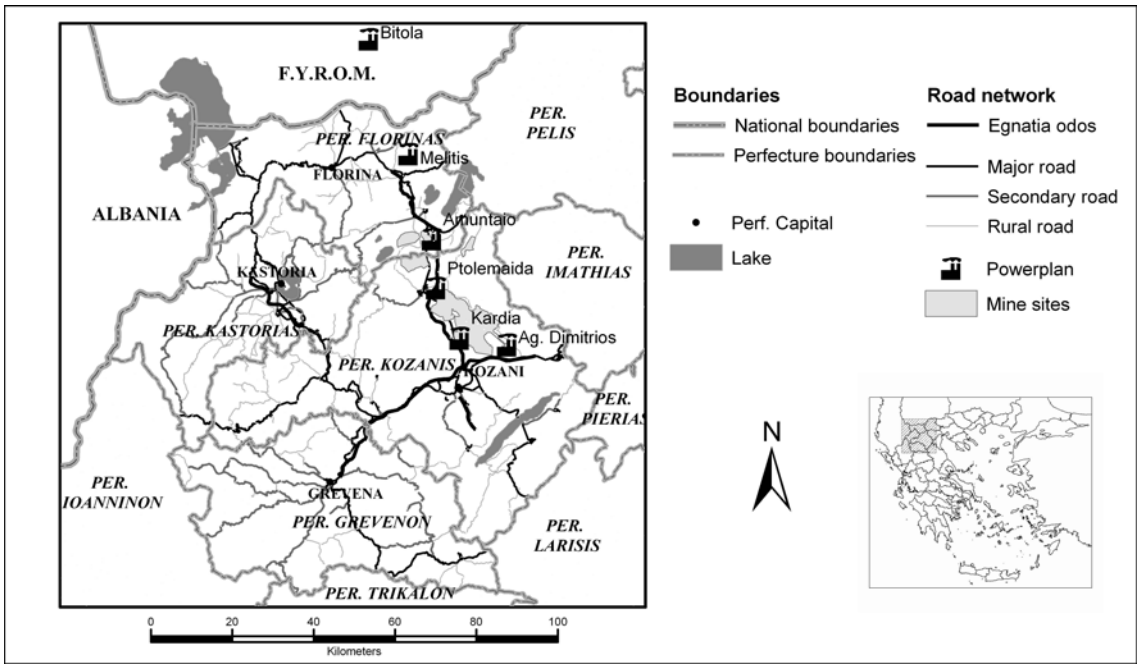


Figure 1. Map of Western Macedonia

2.1 EGU POINT SOURCES

The Greek Public Power Corporation (PPC) operates 5 thermal power plants in the area (Table 1). Furthermore, approximately 20 km from the border between FYROM and Greece, the Bitola thermal power station operates. The station significantly influences the atmospheric quality of the northern cities of West Macedonia in the event of north winds.

Table 1. Yearly emissions from EGUs. (EPER)

EGU	Capacity	Energy	SO_2	NO_x	PM10	CO
	MW	MWh	tn / year	tn / year	tn / year	tn / year
AG. DIMITRIOS	1595	11481875	6950	21600	19900	5540
KARDIA	1250	9107935	11700	19900	4560	2290
PTOLEMAIDA	620	3784147	14000	7640	4050	2820
AMYNTAIO	600	3853170	35800	7500	1830	5060
MELITI	330	2218250	3010	1990	238	-

2.2 MINING ACTIVITIES

Lignite is the main fuel of the thermal power stations in the area, which is excavated from the nearby open mines (Fig. 1). The total production is over 50 million tons/year produced from 250 million cubic meters of overburden and interbedded sediments (Kolovos et al 2003). Thus far there are not any direct measurements or estimates of the emissions of the mines, and studies are currently under preparation.

2.3 HEATING

In Western Macedonia central heating fuel is predominantly oil. In small villages and isolated dwellings, wood is burned for heating. Additionally, in the main cities neighboring with power plants (Kozani, Ptolemais and Amyntaio) a district heating exists that covers most parts. The emissions from heating are estimated from (Baldasano, 1998) taking into consideration the total heating oil consumed in the four prefects of the region from the Greek Statistics Office.

2.4 TRAFFIC

Road traffic emissions are an important factor for the majority of the urban areas. In the present study a gross amount of traffic related emissions was provided from the Ministry of Environment. The major roads of the domain (including Egnatia road) are treated as line sources where as the rest as area. The emission from the line sources was spread over the domain according to the road network, whereas the rest mapped according to a land cover based weighting factor described in IMPRESAREO (Winiwarter et al., 2003). The bulk traffic emissions are located on the new Egnatia road crossing the region and the urban establishments.

2.5 BIOGENIC

For the estimation of the biogenic emissions, the GLOBEIS 3 (Yarwood et al. 1999) model was applied. The inputs to the model are existing high resolution land cover data classified according to the BEIS categories, monthly mean fractional cloud cover and ambient air temperature from the Greek Met Office and VOC speciation for the CB4 chemical mechanisms. The main biogenic emissions are located in the west part of region where large forest environments exists.

2.6 INTEGRATION

The emissions from all categories were combined into a single emission inventory for each pollutant merging the computed data into the ARC GIS environment. The produced inventories on an annual basis are presented in Fig 2. The main emission sources from the area are related to the electricity production facilities (mining and thermal power plants). Also significant contribution is estimated from the traffic especially in the main cities of the region.

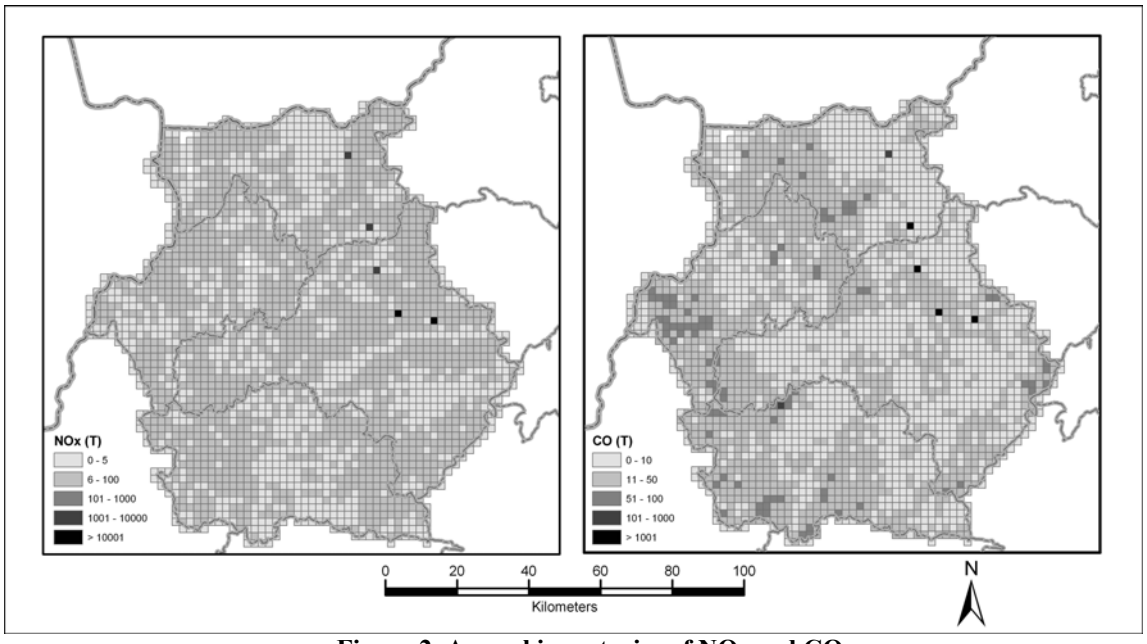


Figure 2. Annual inventories of NO_x and CO

3. CONCLUSIONS

The compilation of a highly detailed spatial emission inventory for the region of Western Macedonia, Greece is presented. The area is dominated from emissions of the electricity production facilities (thermal power plants and mining activities) and traffic especially in the main cities of the area. The reported pollutants are NO_x, CO, SO_2, PM and VOC.

4. ACKNOWLEDGEMENTS

The present work is funded from the 3rd Western Macedonia Regional Fund.

5. REFERENCES

Baldasano J.M., (ed). 1998 Air Pollution Emissions Inventory. Guidelines and formulation of an ungrade source emission model for atmospheric pollutants. U.K: Computational Mechanics Publications.

EPER, European Pollution Emission Registry, Greece data for 2004.

Kolovos, N., et. al. 2002, Utilization of lignite reserves and simultaneous improvement of dust emissions and operation efficiency of a power plant by controlling the calcium (total and free) content of the fed lignite. Application on the Agios Dimitrios Power Plant, Ptolemais, Greece, Energy and Fuels 16 (6), pp. 1516-1522

Papadakis, N., et al., 2002. Environmental conditions and health within the county of Kozani. 1st Environmental Conference of Macedonia, Thessaloniki 2003, pp. 254-261

Samara C. 2005 Chemical mass balance source apportionment of TSP in a lignite-burning area of western Macedonia, Greece. Atmospheric Environment 39, 6430-6443.

Sichletidis L, et al, 2005 The effects of environmental pollution on the respiratory system of children in Western Macedonia, Greece, J Invest Allergol Clin Immunol, 15(2): 117-123

Triantafyllou A. 2000 Patterns and concentrations of PM10 in a mountainous basin region. J. Air & Waste Management Association 50,1017-1022

Winiwarter W., et al., 2003. Methods for comparing gridded inventories of atmospheric emissions - Application for Milan province, Italy and the Greater Athens Area, Greece. The Science of the Total Environment, 303, pp 231-243

Yarwood, G., G. Wilson, C. Emery, and A. Guenther. 1999. Development of GloBEIS – A State of the Science Biogenic Emissions Modeling System. Final Report. Prepared for Texas Natural Resource Conservation Commission.

CARBON AND OXYGEN ISOTOPE COMPOSITION OF ANTHROPOGENIC CO_2 SOURCES IN THE URBAN ENVIRONMENT

M. Zimnoch, M. Mlicki, K. Rozanski
Faculty of Physics and Applied Computer Science, AGH University of Science and Technology,
Al. Mickiewicza 30, 30-059 Krakow, Poland

ABSTRACT

Stable isotope composition of CO_2 originating from various anthropogenic urban sources was investigated. The CO_2 sources were classified into three categories: (i) cars of different make (ii) domestic heating systems relying on methane burning (low emission), and (iii) centralized heating systems relying on coal burning in plants producing both heat and electricity (high emission). The measurements revealed three well-defined groups with respect to carbon isotope composition ($\delta^{13}C$): -30.6±0.26‰ (car traffic), -23.8±0.08‰ (coal burning) and -50.7±0.28‰ (methane burning). The oxygen isotope composition ($\delta^{18}O$) of CO_2 varied in a broad range, from ca. -11‰ to ca. -23‰, the most negative values being observed for coal and methane burning. The $\delta^{18}O$ values of CO_2 from car exhausts occupy less negative portion of the above indicated range and in general differ significantly from car to car.

1. INTRODUCTION

Attempts to quantify the role of urban areas in the global carbon budget have so far focused mainly on inventories of emissions originating from burning of fossil fuel and from cement production, complemented by the assessments of carbon sequestration based on urban biomass estimates (Grimmond et al., 2002). The emission data based on inventories have a number of limitations in terms of their temporal and spatial resolution, and tend to rely on simplified assumptions linking specific activities to expected carbon dioxide fluxes. Thus, alternative ways of assessing carbon dioxide fluxes and their temporal and spatial variability for range of urban environments are needed.

Observations of atmospheric CO_2 mixing ratios alone do not provide information on apportionment of biogenic and fossil-fuel related sources of CO_2. Several methods have been employed to address this question. The methods based on the isotopic composition of atmospheric CO_2 are considered most reliable. Isotopic investigations of atmospheric CO_2 can be particularly useful when studying the carbon cycle in heavily polluted urban areas, with high input of carbon dioxide from fossil fuel burning (heating, car traffic) and from industrial activities (Levin et al., 2003; Kuc et al., 2007). The method utilizing stable isotope composition of CO_2 for apportionment of biogenic and fossil-fuel related CO_2 sources in urban environment requires input data on carbon and oxygen isotope composition of various sources of this gas (Clark-Thorne and Yapp, 2003; Zimnoch et al., 2004).

The primary aim of the presented study was to provide some background data on carbon and oxygen isotope composition of major anthropogenic CO_2 sources. The study was carried out in Krakow, a second largest city in Poland. With about 1 million inhabitants, rapidly growing car traffic and significant industrial activities, it represents a typical urban environment. Coal, gas, and oil consumed for communal and transport purposes generate the main flux of anthropogenic carbon dioxide within the region. In addition, Krakow region is under substantial influence of a large coal mining and industrial centre (Upper Silesia) located approximately 60 km west of the city.

2. METHODOLOGY

A special mobile sampling device was constructed which allows sequential, *in situ* collection of several samples of exhaust gases (Fig. 1). The samples were collected directly from exhaust pipes of various CO_2 sources. The sampled exhaust gases were pumped through a two-step drying system consisting of the Nafion tube immersed in silicagel and of additional trap filled with magnesium perchloride. Two 500-ml glass flasks were used as storage volumes. Prior to sampling, the collection flasks were flushed with the exhaust gases for approximately 10 min. One pair of samples was collected for each type of CO_2 source. In the laboratory, the CO_2 was separated cryogenically from the collected exhaust gases. Three extractions were made for each collected sample. The carbon and oxygen isotopic composition of CO_2 was then analysed using Finnigan Delta-S mass spectrometer and expressed as relative deviations from the internationally accepted standard. The isotope results are reported on the VPDB-CO_2 scale (Allison et. 1995). Gaseous mixtures prepared from synthetic air and CO_2 of known isotopic composition were employed to test the extraction method for presence of systematic errors and to assess the overall uncertainty of the isotope analyses performed. The resulting uncertainty including extraction and mass spectrometric analysis turned out to be in the order of 0.08 ‰ and 0.07 ‰ for $\delta^{13}C$ and $\delta^{18}O$, respectively (Mlicki, 2000).

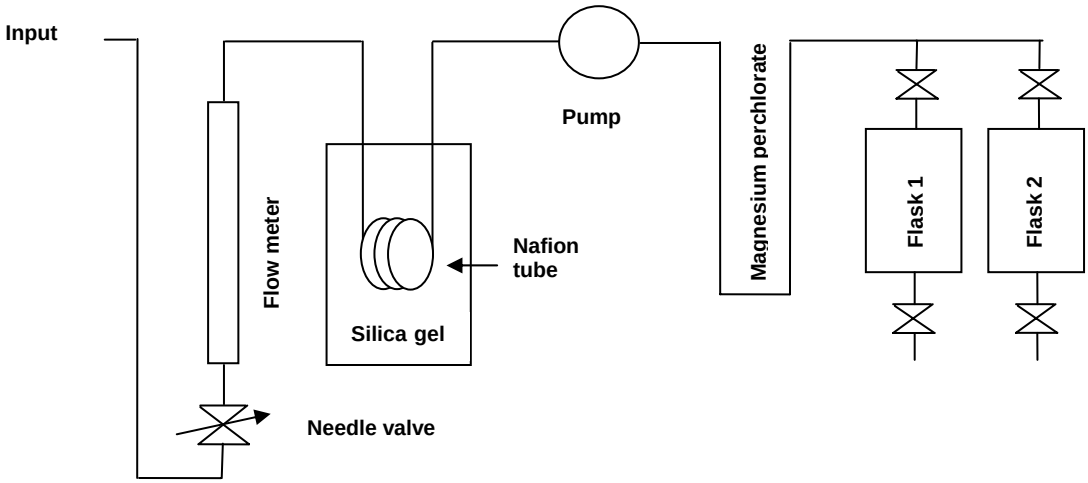


Fig.1. Schematic diagram of a mobile sampling unit used to sample exhaust gases for stable isotope analyses of carbon dioxide. Removable glass flasks allow collection of several samples of exhaust gases during a single sampling campaign.

3. RESULTS AND DISCUSSION

A survey of isotopic composition of different urban anthropogenic CO_2 sources has been carried out during summer months of 2000. The investigated CO_2 sources were classified into three categories: (i) cars of different make (ii) domestic heating systems relying on methane burning (low emission), and (iii) centralized heating systems relying on coal burning (high emission). The first group was further subdivided with respect to the type of engine, presence of catalyst and the type of fuel used. The results of isotope analyses averaged by category are reported in Table 1, while individual data by source are presented in Fig.2.

Table 1. Mean carbon and oxygen isotope composition of the investigated sources of anthropogenic CO_2

Type of CO_2 source **	$\delta^{13}C$ (‰VPDB)	$\delta^{18}O$ (‰VPDB-CO_2)
Diesel engines without catalyst (5)	-30.95 ± 0.06	-19.57 ± 0.18
Gasoline engines without catalyst (5)	-29.24 ± 0.36	-16.33 ± 0.45
Gasoline engines with catalyst (5)	-31.06 ± 0.13	-13.11 ± 0.83
LPG engines without catalyst (2)	-31.88 ± 0.72	-19.82 ± 0.70
LPG engines with catalyst (3)	-30.64 ± 0.28	-11.59 ± 0.75
Low emission -methane burning (5)	-50.72 ± 0.28	-21.68 ± 0.23
High emission - coal burning (3)	-23.80 ± 0.03	-20.53 ± 0.16

** number of samples collected for each type of CO_2 sources is given in parenthesis. Each sample has been analysed three times. The mean isotope composition and its standard deviation is reported for each group.

The carbon isotope composition of CO_2 emitted by different types of sources investigated in the framework of this study turned out to be well-defined. The data presented in Table 1 reveal three distinct groups of $\delta^{13}C$ values. The CO_2 emitted by cars is characterized by uniform $\delta^{13}C$ values, around -30.8 ‰ , irrespectively of the type of engine. Slightly higher $\delta^{13}C$ values (around -29 ‰) were obtained for gasoline engines without catalyst. These cars are using so-called universal fuel mixed with alcohol which is produced from corn or potatoes and is characterized by $\delta^{13}C$ values of around -25‰. Spread of individual $\delta^{13}C$ data within the given group is distinctly smaller for gasoline or LPG engines with catalyst, when compared to cars without catalyst. Also diesel engines reveal relatively small spread of individual data. This might stem from more complete burning of fuel and lower CO/CO_2 ratio for the cars with catalyst. The CO_2 associated with burning of methane in domestic heating systems reveals very low $\delta^{13}C$ values (around -51‰), while burning of coal in industrial plants supplying heat and electricity to the town yields CO_2 with distinctly higher $\delta^{13}C$ values (around -23.8‰).

The $\delta^{13}C$ values of CO_2 associated with burning of coal and methane are similar to that measured directly for the respective fuels. Carbon isotopic composition of coal all over the world varies in a narrow range, between -22‰ and -25‰. The coal being mined in Poland is characterized by $\delta^{13}C$ values from -23.8±0.5‰

to -24.7±0.4‰ (Kotarba, 1988). $\delta^{13}C$ values of methane reveal higher variability, depending on the origin (microbial or thermogenic). Direct, regular measurements of methane present in the city gas network of Krakow, carried out during the period 1995-1996, revealed rather homogeneous isotopic composition of carbon in methane with the mean $\delta^{13}C$ value equal -54.42 ± 0.16‰ (Miroslaw, 1997).

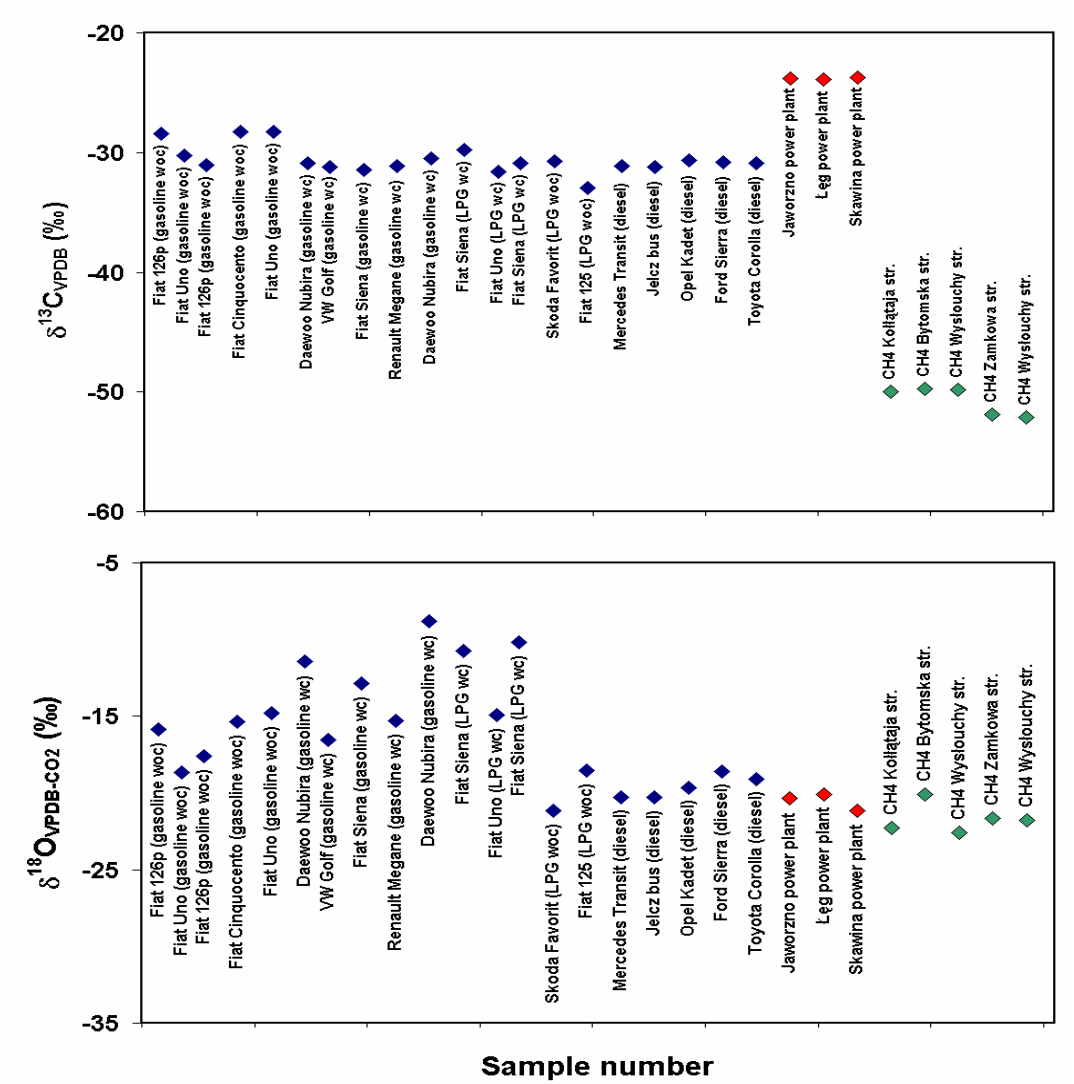


Fig.2. Carbon (upper graph) and oxygen (lower graph) isotope composition of CO_2 extracted from exhaust gases collected from different sources within Krakow urban area. Blue symbols - various makes of cars (identified by labels); red symbols – emission from power plants operating within or in the immediate vicinity of Krakow (CO_2 collected directly from the stack); green symbols – emission point sources representing house heating systems within the city, identified by street names (CO_2 collected directly from chimneys); woc – without catalyst, wc – with catalyst.

Oxygen in CO_2 originating from different anthropogenic sources of this gas stems predominantly from air. The isotopic composition of atmospheric oxygen is uniform and its $\delta^{18}O$ value is equal +23.5 ± 0.3‰ when reported on VSMOW scale (Croopnick and Craig, 1972). When converted to VPDB-CO_2 scale, this value becomes -17.27‰.

The measured $\delta^{18}O$ values range from -8.8‰ (Daewoo Nubira with catalyst) to -22.6‰ (low emission, Wyslouchy street). In general, the measured $\delta^{18}O$ values for gasoline and LPG cars are much more variable than those observed for diesel cars. Mean $\delta^{18}O$ value for diesel cars is equal -19.57 ± 0.18‰ and is comparable with CO_2 emissions associated with methane burning (-21.68 ± 0.23‰), as well as with coal burning (-20.53 ± 0.16‰). Similarity of the $\delta^{18}O$ values and relatively small spread of data suggest stable burning conditions in the presence of surplus of oxygen. Both more negative and less negative $\delta^{18}O$ values are observed, when compared to the $\delta^{18}O$ value of atmospheric oxygen reservoir. Carbon dioxide emitted by cars with catalyst is enriched in ^{18}O when compared to atmospheric oxygen, while other sources are depleted

in ^{18}O isotope.

4. CONCLUSIONS

The reconnaissance study aimed at providing background data on carbon and oxygen isotope composition of CO_2 originating from various anthropogenic sources of carbon present in a typical urban environment revealed substantial variability in both $\delta^{13}C$ and $\delta^{18}O$ values. Three distinct groups of $\delta^{13}C$ values characterizing different sources of CO_2 have been identified: car traffic (around -30.8 ‰), emissions associated with burning of methane in domestic heating systems (around -51‰) and burning of coal in industrial plants supplying heat and electricity to the town (around -23.8‰). All these three sources contribute to the overall carbon budget in the urban atmosphere and modify the ^{13}C isotope signature of free-air background carbon dioxide.

The oxygen isotope composition of CO_2 emitted from various anthropogenic urban sources also revealed wide range of delta values, indicating that the emitted carbon dioxide can be enriched or depleted in ^{18}O when compared to atmospheric oxygen reservoir. This depletion amounts to 3.4‰ for CO_2 from coal and methane burning. Cars with catalyst yield CO_2 which has more variable $\delta^{18}O$ values, being in general more enriched in ^{18}O when compared to atmospheric oxygen.

5. ACKNOWLEDGEMENTS

Partial financial support of this work through the statutory founds of the AGH University of Science and Technology (Project No. 11.11.220.01) as well as the EU project CARBOEUROPE-IP, is kindly acknowledged. The authors wish to thank H. Mroz and Z. Gorczyca for mass-spectrometric measurements.

6. REFERENCES

Allison, C. E., Francey, R. J. and Meijer, H. A. J. 1995 in *Reference and Intercomparison Materials for Stable Isotopes of Light Elements,* IAEA-TECDOC-825, pp. 155-162.

Clark-Thorne, S.T., Yapp, C.J. 2003. Stable carbon isotope constraints on mixing and mass balance of CO_2 in an urban atmosphere: Dallas metropolitan area, Texas, USA, App. Geochem. 18, 75–95.

Grimmond C.S.B., T.S. King, F.D. Cropley, D. Nowak and C. Souch. 2002. Local-scale fluxes of carbon dioxide in urban environments: methodological challenges and results from Chicago. Environmental Pollution, 116, S243-S254

Kotarba, M. 1988. Geochemical criteria for the origin of natural gases accumulated in the upper carboniferous coal-seam-bearing formations in Walbrzych coal basin. Zeszyty Naukowe, 1199, AGH University of Science and Technology, Krakow, (in Polish).

Kroopnick, P., Craig, H. 1972. Atmospheric oxygen: isotopic composition and solubility fractionation. Science, 175, 54-55.

Kuc, T., Rozanski, K., Zimnoch, M., Necki, J., Chmura, L., Jelen, D. 2007.Two decades of regular observations of $^{14}CO_2$ and $^{13}CO_2$ content in atmospheric carbon dioxide in central Europe: long-term changes of regional anthropogenic fossil CO_2 emissions. Radiocarbon, 49(2), 358-375.

Levin, I., Kromer, B., Schmidt, M., Sartorius, H. 2003. A novel approach for independent budgeting of fossil fuels CO_2 over Europe by $^{14}CO_2$ observations. Geophys. Res. Lett. 30, 2194-2198.

Mlicki, M. 2000. Isotope Identification of Anthropogenic Sources of Carbon Dioxide in Krakow. Master Thesis, AGH University of Science and Technology, Krakow, (in Polish).

Mirosław J. 1997. Isotopic Composition of Methane in Atmosphere over Krakow. PhD Thesis, AGH University of Science and Technology, Krakow, (in Polish).

Zimnoch, M., Florkowski, T., Necki, J.M., Neubert, R.E.M., 2004. Diurnal variability of $\delta^{13}C$ and $\delta^{18}O$ of atmospheric CO_2 in the urban atmosphere of Krakow, Poland. Isotopes in Environmental and Health Studies, 40(2), 129-143.