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“ Palladium- a possible tracer for traffic emissions“

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unter der Anleitung von

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1. Introduction:

Several medical studies (Ostro,1993; Dockery et al., 1993) have proven, that a correlation between particulate matter concentrations and the number of daily deaths and hospitalisations of people suffering from pulmonary and cardiac diseases exists. The correlation to morbidity increases further by taking PM 10 and PM 2.5 concentrations into account, because particles of this size can easily be absorbed in the aveolar region of the lung (Hileman, 1981) and have higher concentrations of trace metals like Pb, Cd, Zn, Cr, Ni, Mn (Natusch et al., 1974; Hlavay et al., 1992). These trace metals adsorbed on ambient particles were found to produce tissue damage in the lung (Dreher et al., 1997). Due to the implication of the results of these studies the European Commission has included PM 10 limit values for PM monitoring. In stage one a limit value for particulate matter concentrations of 40 µg/m³ for the annual mean was introduced, further a concentration of 50 µg/m³ should not be exceeded more than 35 times. Stage two limit values, which come to effective in 2010, will be even more strict with an annual mean value set at 20 µg/m³, and the aim that PM10 concentration should not exceed 50µg/m³ more than 7 times a year. If concentration levels of pollutants are above their limit or the limit has to be reduced further because of new results from toxicological investigations it is necessary for Public authorities to set right temporary actions like regulations, penalties, temporary closing of old industrial plants, forcing power plants to change their fuel from coal to natural gas etc. and to set right long-term decisions like forbidding the use of old technology, force the use of new air pollution control devices or regulate traffic to decrease the pollution level. To set the economical best and most efficient actions it is necessary to know the contribution of different sources like traffic, heavy industry, power plants to this pollution.

Traffic will be the focus for environmental studies and considerations in future, because it is the only major air pollution source whose activity is expected to increase in future. Air pollution through other sources like heavy industry and power plants is decreasing due to better technology in combustion like LowNO$_x$ burners, increasing efficiency of air pollution control devices like scrubbers and washers for flue gas cleaning, the substitution of coal with natural gas for power plants, and the fact that heavy industry itself is stagnating in developed countries.

For traffic it was possible to reduce SO_2 emissions through the production of gasoline and diesel with a lower sulphur content, as well as it was possible to get hold of NO_x and hydrocarbon emissions with the introduction of the three way catalyst. Lead emissions decreased significantly since the beginning 90s with the ban of lead additives to gasoline. But because of increasing activity traffic still dominates the pollution of urban air and traffic is still recognised as important source of particles and heavy metals (Wrobel et al., 2000, Pakkanen et al., 2001). To reduce emissions from cars further technological adjustments like optimisation of motor management and better aerodynamics are necessary. However, traffic also contributes to particulate matter emissions with the resuspension of road dust which is independent to adjustments in engine technology or exhaust gas cleaning. For governmental actions like quotation of heavy traffic in regions suffering from traffic pollution it is necessary to know the exact contribution of traffic to pollution levels in the environment.

To determine or estimate the amount of pollution coming from different sources several methods have been used. The following section gives a short overview over the models, in addition a comparison of major advantages and disadvantages of the individual techniques is given.

Dispersion models:

To determine the amount of pollutants deriving from different sources usually emission inventories for all relevant sources are made and combined with metrological models to calculate the dispersion of these pollutants. For this method statistical information like emission factors for every source and pollutant is required, the activity of these sources and their spatial distribution, and metrological information on wind speed, humidity and temperature of air masses. Subseqently a computation of the mixing and dilution of the emitted pollutants and the movement of air masses is conducted. These methods have some limitations. Statistical information on activity and emission from sources like households and automotive work machines is difficult to collect and can have a big uncertainty. Furthermore every metrological situation for the imission site has to be taken into account for a correct estimation of the contribution of different sources to the total imission of pollutants.

Most of these models must be calibrated (appropriate mathematical parameters have to be found) and rely therefore on precedent source apportionment studies on receptor oriented methods or dispersion studies with SF_6 or other tracers. Meteorological data like wind speed, wind direction and temperature needed for these simulations is very complex and can have a big uncertainty for short time considerations.

Resuspension, deposition and long range transport, which has been shown to be responsible for a 20 to 50 fold increase of pollutant concentrations in Norway (Aberg et al., 1999) and to lead to pollution in the Arctic and Antarctic regions (Sturges and Barrie, 1989) have not yet been satisfyingly included because of their complex dependencies. Dispersion models can only be used for particles smaller than 2.5 µm because of their gas-like behaviour. (Vardoulakis, 2003)

Emission factors can be obtained for singular cars with dynamometer based studies or for whole traffic fleets with tunnel studies. Some studies have shown (Gertler et al., 1997; Zielinskaya and Fung 1997) that a difference between the results from tunnel studies and dynamometer based studies exists. It is assumed that real world conditions like rough road surface, shaking, driving behaviour, which are neglected in dynamometer based studies and the fact that fleet emissions can be dominated by a small number of older cars (Stedman et al., 1991; Cadle et al., 1997) are the reason for this difference.

Receptor orientated models:

Measurement of isotopic ratios

Another possibility to track down the contribution of different sources to air pollution is to make use of the fact that every source contains an unique isotopic composition. In theory it is possible to calculate the contribution of different sources to pollution when isotopic ratios emitted from these sources are known.

This method was successful in estimating the contribution of long range transport from England or Central Europe to air pollution in Norway. (Aberg et al., 1999). To apply this method on environmental investigations it must be considered that it is necessary to measure as many isotopes as existing sources, and that differences between isotopic ratios can be small. Therefore it is usually necessary to use high resolution mass spectrometry for detection because of good accuracy and more accessible isotopes. This method is inapplicable when the number of isotopes is smaller than the number of possible sources.

Size distribution measurements:

A different approach to assign source contribution to pollution is the determination of particle size distribution of pollutants. (Allen et al., 2001). This method is based on the assumption that the concentration of pollutants over the particle size range differs between sources. Three groups of compounds could be distinguished by this approach: Compounds with their concentration maximum in the coarse particle fraction, which means that their sources are soil and road dust and mechanical abrasion. Compounds of this group are Fe, Na, Sr, Ba and Cl which are part of soil dust and sea salt. Pb, Cd, Sn, Se have been found to have their concentration maximum in the accumulation mode (particles smaller than 0.5 µm diameter), which means that particles containing these elements are formed during combustion. The third group is formed by compounds which has no defined concentration maximum, but a nearly even distribution of their concentration over the whole particle size spectrum, for example K, Cu and Ni. These elements are not only emitted by combustion but also by mechanical abrasion and resuspension of contaminated road dust. So it is possible with this method to differ between the contribution of sources with different emission mechanisms like the primary emission of ultrafine particles from combustion and industrial processes, the resuspension of larger particles and frictionally generated particles (mechanical wear). (Allen et al., 2001)

Multivariate data analysis:

Multivariate data analysis like prime factor analysis and principle component analysis is a statistical tool to split the applied data matrix into independent contributors. The basic assumptions of these statistical methods are that every contributor (source) has its own constant (emission) spectra and that the contribution to different samples has a random variation for every source. This method can be used for pollution data sets to find independent pollution sources which emit different pollution compositions, and to calculate further their contribution to every sample. To obtain good results by this method a data set of about fifty samples and the analysis of several components is necessary. For the interpretation of the results it is necessary to connect these independent sources received by calculation to real emission sources, so some kind of information about relevant sources and their emission composition must be known in advance. The advantage of this statistical methods is that additional information like metrological data, number of considerable sources etc. which can import further uncertainties to the results are not implemented in the model. However, these methods have their limitation. The differences between the emission profiles can be in the magnitude of analytical uncertainties, which makes it impossible for these methods to differ between them. Multivariate data analysis can be incapable to differentiate between primary particles from vehicles, resuspended road dust and soil dust because of their similar composition (Artaxo et al., 1999). The differentiation of sources can also fail if these sources are situated in the same direction relative to the imission site, so that the multivariate data analysis associates these sources during calculation because of the metrological caused correlation of their imission, as happened to several trace metals and sea salt when this method was applied to air pollution measurements in Australia (Cohen et al., 2002).

Chemical mass balance:

The assumptions of this method is, that every source emits a unique pollutant spectra. When these spectra are known for every important source for the sampling site, it is possible to calculate the relative contribution of every source for every pollutant. The data matrix obtained by the calculation of the source is usually fitted to the original data matrix with the least square approach (Cass et al., 1983). Possible interferences are long range transport effects contributing to the pollution levels on the sampling site. Additional uncertainties can arise from the fact that emitted pollution composition might not be constant over time, e.g. the emission of municipal waste combustion was found to be strongly dependent on waste composition (Hasselriis and Licata, 1995) .

Tracer models:

Tracer models are simplified chemical mass balance models. A tracer is a component or element whose emission is dominated by one source and which has a constant content in this source. If the ratios between the emission of this tracer component and other emitted pollutants from this source are known and constant, it is possible to determine the contribution to pollution of the source related to this tracer by simple extrapolation from the measured concentration of this tracer element. To use this approach a tracer component and the emission ratio to other pollutants has to be found for every source influencing the sampling site . This is possible under conditions where it is ensured that pollutants derive only from one source. Optimal for these studies are for example chimneys of power plants, road tunnels and tail pipe measurements for traffic emissions. Good examples for tracer components are silica, iron and manganese (Sternbeck et al., 2002) which can be used as tracer for soil dust because no other source of comparable magnitude for these elements exists. Problems with the tracer approach can only appear, if the tracer shows different chemical or physical behaviour in the environment compared to correlated pollutants. Different particle sizes and therefore different deposition rates and aerodynamic behaviour or different condensation and adsorption behaviour can lead to different concentration ratios between pollutants and the tracer components at the emission and imission site.

Traffic Emissions:

Traffic emits a whole variety of air pollutants. The combustion process itself is the source for several pollutants. Gaseous components like NO_x, organic compounds and black carbon are emitted in concentrations strongly dependent on motor management and the ignition process. Elements like lead, nickel and vanadium are still content in raw oil and therefore found in gasoline combustion products. Break lining wear is the source of several metals like copper, zinc, barium, and lead. Tyre wear is suspected to be the source of antimony and is certainly a source of black carbon, sulphur and zinc. Mechanical abrasion of the car body can also emit particles containing zinc, nickel and other alloy components of steel. Emitted organic and inorganic reactive gases form secondary particulate matter via atmospheric transformation.

In the last decades it was possible to determine the contribution of traffic to the total pollutant levels by using lead as tracer for traffic emissions. Because the amount of emitted lead was far higher than emissions from other sources due to anti knock lead additives to gasoline lead was the ideal tracer element for traffic emissions. But with the ban of these lead additives new tracers had to be found to determine the amount of pollution caused by traffic.

One group of possible tracers are organic trace compounds contained in raw oil. These petroleum biomarkers are molecular structures present in petroleum stemming from the microorganisms which created the deposits (Peters and Moldowan, 1993). These structures including hopanes and steranes are present in lubricating oils and therefore present in particulate matter emitted from gasoline and diesel engines and were used as tracers to track emissions deriving from traffic (Schauer et al., 1996). However, the fact that these compounds are not inert to photochemical reactions and appear in low concentration in ambient air (0.2 ng/m^3 , Fraser et al., 1999) arise problems in using them as tracers for particulate matter emissions from traffic.

The introduction of the three way catalyst in the mid 80´s added new elements to the emission of traffic: the platinum group elements Pt, Pd and Rh. These elements are used in the catalyst as active compounds to facilitate the oxidation of hydrocarbons and other incompletely oxidised components with nitrogen oxides, which leads to a reduction of 90% for the amount of hydrocarbons and nitrogen oxides in the exhaust gas. Even for diesel engines oxidation catalysts are developed and ready to be integrated in new manufactured cars. About 2 g of these platinum group elements per catalyst are situated on the washcoat which cloaks the honeycomb aluminium monolith. Previous investigations have shown that these precious metals are emitted by the catalyst in the ng/km range (Moldovan et al., 2002) and that this is the result of mechanical abrasion of PGM containing washcoat particles. (Palacios et al., 1999) Some sampling campaigns have shown that their concentration in the environment increases since the introduction of the catalyst (Palacios et al., 2000; Moldovan et al., 1999). Another indication for traffic as main source is their decreasing concentration in road dust with increasing distance to the road (Harrison et al., 1997). What makes them to possible candidates for tracer components for particulate traffic emissions is the fact that no other emission sources except some rare used metallurgical processes for these precious metals are known. Even if they are mainly emitted by spark ignition motors nowadays, they can be used as tracer for the emission of pollutants caused by traffic, because when the composition of the car fleet is known it is possible to recalculate expected palladium emission ratios for the whole car fleet.

The present study was conducted to determine emission factors of palladium and other components emitted by cars and to proof the usability of Pd as tracer for automotive emissions.

2. Experimental

2.1 Sampling

Sampling strategy:

To determine the emission rates of individual particulate motor vehicle emissions a road tunnel study was performed in September 2002 in the Kaisermühlen tunnel. The ratio between pollutants and palladium emissions should be calculated from the emission factors obtained from these tunnel measurements. For calculating the emission factors tunnel outside and tunnel inside samples were taken. To proof the usability of Pd as tracer for particulate traffic emissions sampling campaigns were conducted in Vienna and in Oberwart (chapter 5.1). Samples were analysed for particle mass (PM), total carbon (TC), black carbon (BC), several trace metals typically emitted by traffic - Zn, Cu, Pb, Ni, V - and Pd as the tracer component.

The Kaisermühlen tunnel:

The Kaisermühlen tunnel is part of the A21 highway which passes through Vienna along the Danube (Fig. 1). The tunnel length is 1.7 km, it consists of two separate tubes for each traffic flow direction and three driving lanes per tube. The speed limit is 80 kmh^{-1}. The traffic density is 50000 vehicles per day and direction with a mean of 13 % heavy duty vehicles in the car fleet on workdays and 7 % during the weekend. The ventilation inside the tunnel is produced by car movement only. Air velocity and traffic are continuously monitored by the Autobahnmeisterei Kaisermühlen. The data on traffic density and air velocity inside the tunnel was provided by the MA 32 of the city of Vienna.

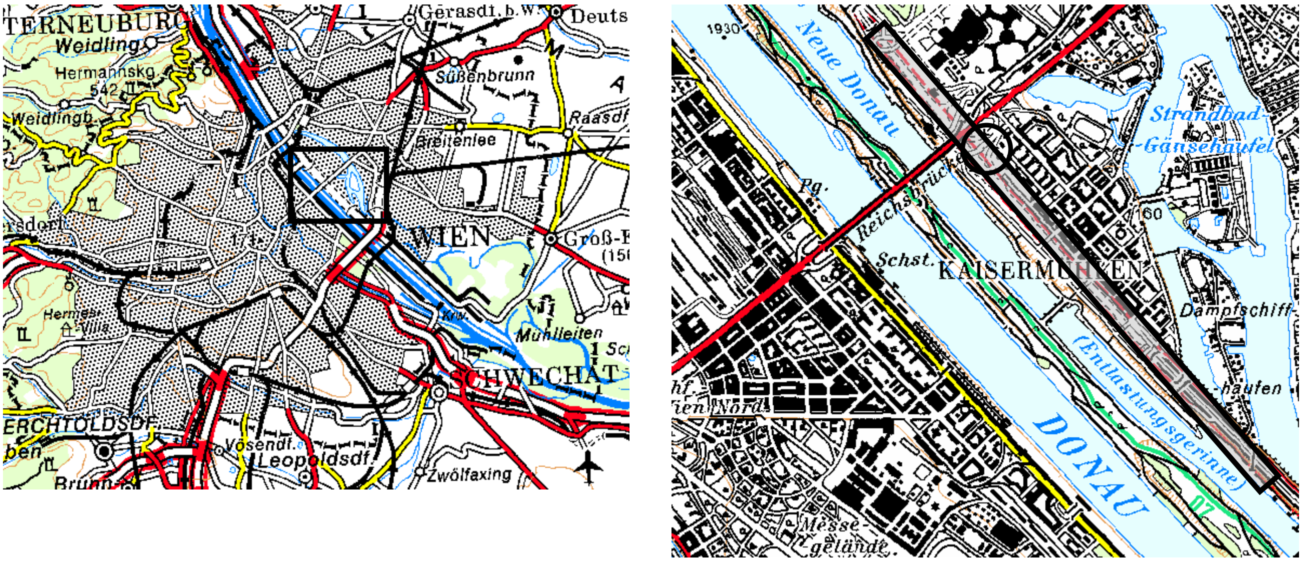


Fig. 1 Geographical location of the Kaisermühlen tunnel

Tunnel Inside and outside measurements were equipped with three sampling lines (Fig. 2). One sampling line consisted of a membrane pump (N010KN 18) with a flow of 7.5 l min^{-1} and a quartz fibre filter (Pallflex membrane filter-Tissuequarz 2500Qat-UP), for the two other lines cellulose ester filters (Pall-Metricel Membrane filter 47 mm 0.8 µm) and a membrane pump respectively a rotary vein were used with a flow of 30 and 52 l min^{-1}. Sampling was performed between the 18th of September and the 7th of October 2002, filters were changed between 8 and 9 o clock in the morning after 24 h for inside measurements and after 48 h for outside measurements.

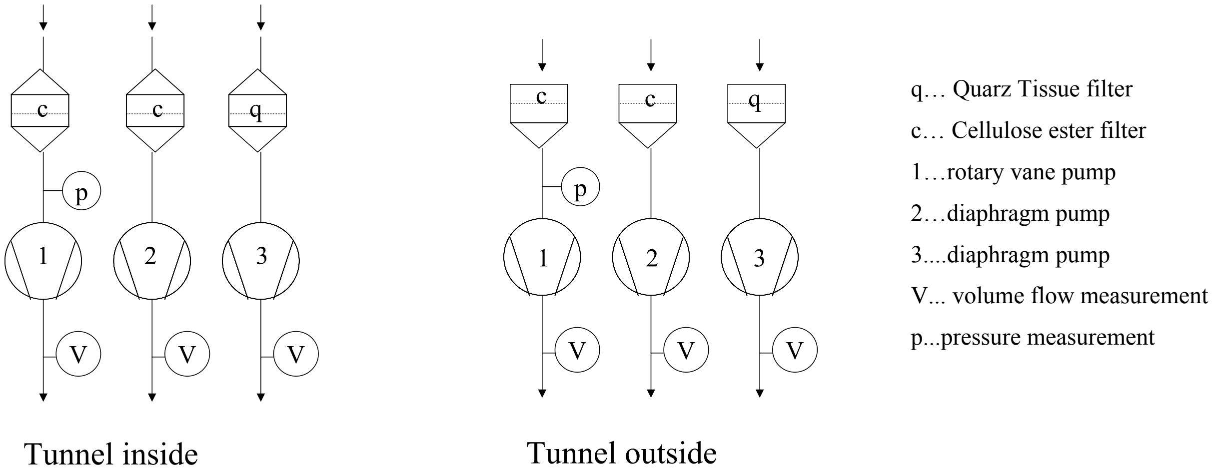


Fig. 2 Constitution of the sampling lines for the Kaisermühlen tunnel

Inside samples were taken in the fire fume ventilation (Fig. 3, Pic. 1), which is situated above the ceiling of the tunnel at approximately 8 m height. For inside measurements the filter heads were equipped with 20 cm long Teflon tubes (15 mm diameter) which were stuck through a grid at the bottom of the exhaust fume

Outside measurements were conducted with an open face design at the outlet of the fire fume ventilation pointing at the Danube bank (Fig. 3, Pic. 2), because neither electricity nor amenability was available at the tunnel entrance. The whole sampling site was weather protected.

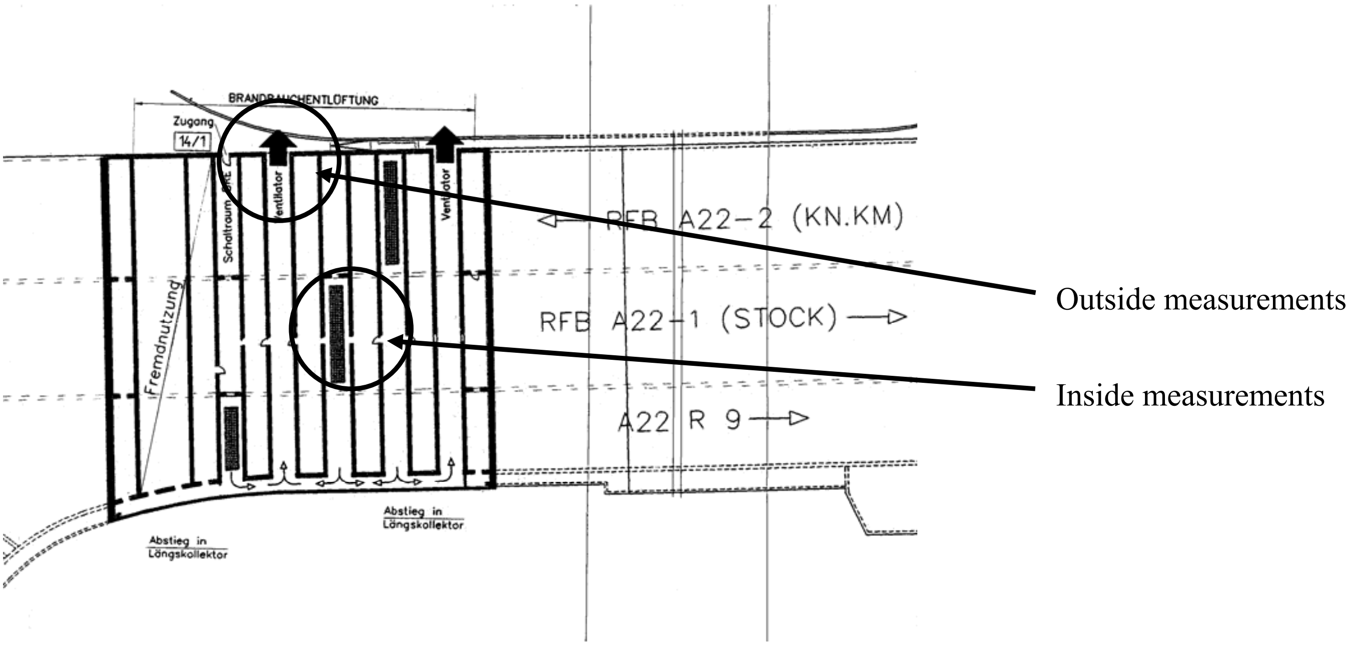
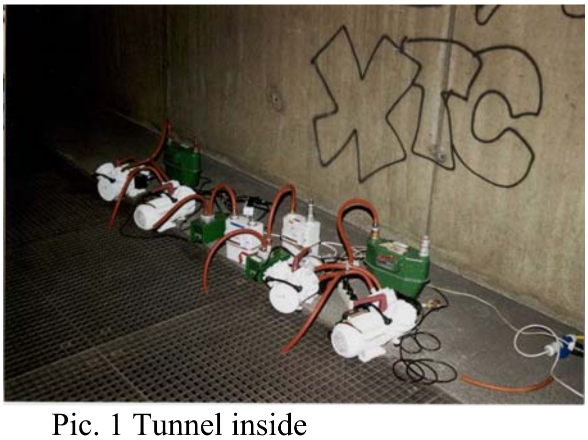


Fig. 3 Plot of the fire fume ventilation of the Kaisermühlen tunnel



Pic. 1 Tunnel inside

Pic. 2 Tunnel outside

2.2 Sample treatment and detection:

The quarz fiber filters were used for total carbon, black carbon and trace metal analysis, the cellulose ester filters were used for aerosol mass determination and palladium analysis.

Aerosol mass:

Gravimetric analysis of cellulose ester filters were performed with a microbalance (Sartorius M5P-000V001) after 2 h equilibration at 23 °C and 50 % relative humidity. Sample filters were weighted before and after sampling, the mass difference was the amount of sampled particulate matter.

Total Carbon (TC)

The total carbon amount was determined with a combustion method similar to the procedure described by Puxbaum and Rendl (1983). An aliquot of the quartz filter (Ø 9 mm) was combusted in an oven at 1000 °C under a steady oxygen stream provided by a mass flow controller (Bronkhorst). The formed amount of CO_2 was analysed by a Non-Dispersive Infrared (NDIR) analyser (Maihak Sifor 200). Quartz field blanks were treated and analysed like quartz filter samples.

Black carbon: (BC)

For the analysis of Black carbon a quartz filter aliquot (Ø 9 mm) was treated with a combustion step at 320 °C for two hours under a steady oxygen steam The purpose of this treatment is the complete decomposition of organic compounds. The amount of the remaining elemental carbon was analysed as described for total carbon

Organic carbon (OC):

Organic carbon is defined as the amount of carbon combusted in the first combustion step of the determination of black carbon. Thus the amount of organic carbon is the difference between the determined amount of total carbon and the amount of black carbon.

Trace Metals:

The quartz filter was parted with ceramic scissors, the exact size of the parts has been determined gravimetrically. For the decomposition of the collected aerosol the filter piece used for trace metal analysis was decomposed in a Teflon bomb with 0.5 ml of concentrated nitric acid at 180 °C for 2 h. Afterwards the solution was diluted with 5 ml of distilled water and the remaining filter components were separated by centrifugation. Cu, Pb, Ni, V were measured with Perkin Elmer 4100-ZE ET-AAS and a sample volume of 20 µl. Temperature programs were optimised for peak height and matrix separation. The determination of Zn was conducted with Perkin Elmer 403 flame-AAS. Field blanks were analysed like samples.

Palladium:

Independent from how analytical technique used for determination it is necessary to digest aerosol samples completely to receive liquid sample solutions. For a complete dissolution of palladium a two step digestion procedure was applied. In the first step cellulose ester filters and the aerosol were digested as a whole with 2 ml concentrated nitric acid at 180 °C for 2.5 hours in Teflon bombs. Afterwards 50 µl of fluoric acid were added to each sample to volatilise probably existing silica material, and 50 µl of perchloric acid were added to ensure a complete oxidation of elemental carbon and palladium. Nitric and fluoric acids were removed at 150 °C. The remaining droplet of perchloric acid solution was diluted with 5 ml of 10% hydrochloric acid, the solution was then homogenised and analysed with FI-ET-AAS procedure to provide further matrix separation and a preconcentration of palladium. A more detailed description of this procedure can be found in Limbeck et al. (2003). Field blanks were treated like samples.

Reagents and standard solutions

High purity water was obtained by distillation of deionised water in a quartz apparatus. Nitric acid (HNO_3), hydrochloric acid (HCl), methanol and ethanol were of p.a. grade purity (Merck, Darmstadt, Germany). Perchloric acid ($HClO_4$) as well as hydrofluoric acid (HF) were of suprapur grade quality (Merck, Darmstadt, Germany). The complexing agent for palladium (N,N-diethyl-N´-benzoylthiourea, DEBT) was prepared from benzoyl-isothiocyanate and aminoethanol and recrystallized with ethanol. All standard solutions were prepared by appropriate dilution of stock solutions with 10% HCl for palladium standards respectively with 10% nitric acid for trace metal standards just before use.

Calculation of concentrations:

Concentrations of the detected solutions were calculated using a linear calibration curve. Afterwards mean values from field blanks were subtracted. The amount per filter was calculated for every compound regarding the dilution occurring during the sample treatment. The amount was then divided through the normalised volume passing through the filter during the sampling period to obtain the concentration in the sampled air.

2.3 Detection limits and analytical uncertainties:

The total error of the determined concentrations is the sum of all errors that occur from sampling to analysis. In the following section the errors from analysis, sample treatment and sampling were estimated.

Standard deviation of the analytical procedure and corresponding detection limits:

Detection limits were calculated using the 3 σ criteria with standard deviations obtained from the measurement of standard solutions. Afterwards the detectable amount for every compound per filter was calculated regarding the dilution occurring during the sample treatment.

To calculate the Relative standard deviation of the analysis the standard deviation which was derived from the measurements of standard solutions was divided through the average sample concentration.

Table 1 presents the derived results for the investigated aerosol constituents.

	Aerosol mass	Carbon parameters	Zn	Cu	Pb	Ni	V	Cd	Pd
detection limit in solution		µg per aliquot	ppb						Ppt
		3	10	1	0.5	2.5	1	0.2	40
Detection limit per filter	mg	µg	ng						Pg
	0.06	62	110	11	5.5	27.5	11	2.2	200
relative standard deviation (%)	0.5	4	5	7	2.5	11	5	3	5.6

Tab.1 Standard deviation of detection and detection limit

Sample treatment:

Measurement of carbon parameters:

A filter aliquot (Ø 9 mm) was analysed for total carbon respectively for black carbon. Assuming that the filter was covered homogenous with aerosol and that diameter of the sampled filter area is Ø 41 mm. An error of 1 mm in the diameter of the filter area covered by aerosol leads to a relative error of 5 % for the calculation of the total amount of total and elemental carbon per filter.

Trace metals:

The error made during the dilution of the digested sample can be neglected regarding other uncertainties. Errors which can occur during the digestion step are that the aerosol is not completely digested or that an amount of the trace metals is adsorbed on the surface of remaining quartz fibres. The sum of the relative deviation in the sample treatment from obtaining the samples to the detection step, including the digestion procedure, was estimated for all of these trace metals to be in the range of the relative standard deviation of AAS measurements at 5 % .

Measurement and calculation of the gas volume:

The gas volume was normalised to standard temperature an standard pressure. The gas meters (Elster BK 2.5) had a maximum relative deviation of 1% according to the manufacturer. Errors concerning the temperature were estimated to 0.5 %. The error made for the pressure measurement was estimated to be 2 %, which makes a total relative deviation of the gas volume determination of 1.5 % for sampling lines equipped with diaphragm pumps and 3.5 % for sampling lines equipped with rotary vein pumps.

Total relative standard deviation caused by sampling and sample treatment:

The relative error of the obtained concentrations is the sum of all relative errors made in sampling, sample treatment and detection For all measured components except the aerosol mass an error of around 10 % was obtained (Tab. 2).

	Aerosol mass	Carbon parameters	Zn	Cu	Pb	Ni	V	Cd	Pd
Total relative error (%)	0.5	10.5	11.5	13.5	9.0	17.5	11.5	9.5	12.1

Tab. 2 Summed relative errors

3. Results

3.1 Aerosol composition

Atmospheric aerosol:

Atmospheric aerosol is built up by several components, the major constituents are sulphate carbonaceous components the mineral fraction including the trace elements and the aerosol humidity these of components could be of primary origin, which means that these compounds are emitted in the particulate state, like resuspended soil and road dust fly ash or particles formed by mechanical abrasion e.g. tyre and break lining wear. black carbon and aerosol deriving from nature like pollen and fungal spores. Gaseous emitted precursors form after chemical or physical transformation e.g. oxidation or salt formation the secondary aerosol in the atmosphere. The main components of the secondary aerosol are nitrates, sulphates, ammonia salts and organic compounds. The carbonaceous part of the aerosol can be divided into inorganic carbonates, black carbon, and organic carbon. Black carbon is formed by incomplete combustion and is emitted from big diesel engines, uncontrolled fires, power plants and households. Primary organic carbon aerosol consists of nature derived pollen and fungal spores, secondary organic aerosol is formed by various compounds like carboxylic acids and other oxygenated organic compounds.

Trace metals:

Typically 1 % of the aerosol mass is built up by various trace metals. Their concentration in ambient air is in the ng/m³ range. These trace metals are mainly emitted by metallurgical processes, mechanical abrasion or the combustion of materials containing these metals e.g. oil, coal and municipal waste.

Zn:

Major sources for Zn in the aerosol are tyre wear (2 % of the tyres is made up by ZnO), break linings and car bodies from vehicles, metal industry, municipal waste incineration and coal burning. Zn is a metal used to cloak steel for corrosion prevention, it is also a component in batteries and brass. The oxide (ZnO) is used in the manufacture of paints, rubber products, cosmetics, pharmaceuticals, floor coverings, plastics, printing inks, soap, textiles, electrical equipment, and other products. It is also used in ointments. The sulphide (ZnS) is used in making luminous dials, X-ray and TV screens, paints and fluorescent lights.

Cu:

One of the oldest uses for copper is to form brass and bronze. Copper is a component in coins and wire material. Copper sulphate is used as agricultural poison. The electrical industry is the largest user for copper. Copper is also used in break linings and therefore correlated to air pollution caused by traffic. Sources of copper emissions are traffic, coal combustion, waste incineration and metal industry.

Pb:

Lead and its oxide is used to store electricity in car batteries. Pb(Et)4 was widely used as anti-knock additive for gasoline and banned in the 90s. Lead is still content in fossil energy sources like coal and raw oil and also found in wood (Nriagu and Pancaya, 1988) and therefore emitted by combustion processes and also related to traffic pollution. Other uses for lead are X-ray absorption, cable covering and as additive for special glasses.

Ni:

Nickel is mainly used as alloy component in stainless steel and other corrosion resistant alloys, and is widely used in coinage. Certain amounts of nickel are also found in coal and raw oil. Mechanical abrasion of steel, metallurgical processes and combustion of coal and heavy fuel oil are sources for nickel in the aerosol. A part of nickel emissions can therefore be correlated with traffic.

V

Vanadium is used for producing rust-resistant springs and steels used for making tools. About 80 % of the vanadium now produced is used as ferrovanadium or as a steel additive. Vanadium foil is used as a bonding agent in biding titanium to steel. The pentoxide V_2O_5 is used in ceramics and as a chemical catalyst. Vanadium compounds are used for dyeing and printing fabrics. It is also present in some crude oils. The content of vanadium in raw oil is the reason that fuel oil combustion is the largest contributor of vanadium found in the air.

Cd:

Rather like zinc, cadmium is used to a small extent as coatings (often achieved by electroplating) to protect metals such as iron. Its use is restricted because of environmental concerns. The metal is a component of some specialist alloys including solders and alloys with low coefficients of friction and good fatigue resistance. Cadmium is a component of Ni-Cd batteries. Cadmium is used in black and white television phosphors and in blue and green phosphors for colour TV tubes. Some semiconductors contain cadmium. The sulphide (CdS) is used as a yellow pigment. Some compounds are used as stabilizers for PVC.

Pd:

Palladium is mainly used as catalyst for hydrogenation and dehydrogenation reactions and is therefore a component in the three way catalyst. 1.8 mg of platinum group elements are per catalyst are used, one fourth is palladium whose emission for one catalyst is in the ng per km range. Other uses for palladium are jewellery to form white gold, dentistry (crowns) and electrical contacts. The largest emitter of palladium by far is traffic.

Emission situation in Vienna:

Possible sources of these aerosol components in Vienna are traffic, space heating, municipal waste incineration and power plants, but it can be assumed that the influence on air pollution from other sources than traffic and space heating can be neglected because of strict laws regulating the emission from municipal waste incineration and power plants.

3.2 Tunnel outside measurements

The mean particulate matter concentration during the sampling campaign (10 samples) was 52.4 µg/m³, a value found typical for urban areas in other studies (Bilos et al., 2001) . The concentration of total carbon and black carbon was 12.1 µg m^{-3} and 5.5 µg m^{-3}. The relative amount of black carbon in total suspended matter was about 10%, which agrees also with literature data (Artaxo, 1999). Mean trace metal concentrations ranged between 44.5 ng m^{-3} for zinc, 11.5 and 14.9 ng m^{-3} for copper and lead and 1.7 ng m^{-3} and 1.4 ng m^{-3} for nickel and vanadium, concentrations of this range are comparable to concentrations found in recent sampling campaigns as well (Sternbeck et al., 2002; Valiulis et al., 2002) and significantly lower to values found in older studies (Greenberg et al.,1990; Harrison and Jones, 1995). The average palladium concentration found on this site was 4.8 pg m^{-3}, a content of 4 to 14 pg m^{-3} was found in Vienna (Limbeck et al., 2003), values ranging from <0.2 to 14.6 pg m^{-3} were reported for a suburb of Berlin (Tilch et al., 2000), whereas extremely high concentrations ranging from 21.2 to 85.7 pg m^{-3} were found in Rome (Petrucci et al. 2000). For size segregated PM10 samples from the urban air of Göteborg palladium concentrations ranging from 0.1 to 10 pg m^{-3} were found (Rauch et al 2001). The relative standard deviations of measured concentrations were around 50 % of the mean concentration (tab 3) and much higher than the variation of the analysis (chapter 2.3). A significant difference between workday and weekend concentrations could be observed for particulate matter, carbon parameters, zinc, copper lead and vanadium, but not for palladium and nickel (tab 3).

	Pm	TC	BC	Oc	Zn	Cu	Pb	Ni	V	Pd
	µg m^{-3}				ng m^{-3}					pg m^{-3}
Tunnel outside	52.4	12.1	5.5	6.6	44.5	11.5	14.9	1.7	1.4	4.8
σ	*22.3*	*5.5*	*2.8*	*2.9*	*28.6*	*7.2*	*9.6*	*2.0*	*1.4*	*2.4*
Workday	58.5	13.3	6.1	7.2	49.0	12.6	16.6	1.4	1.7	4.9
σ	*23.5*	*6.2*	*3.1*	*3.2*	*32.0*	*8.1*	*10.8*	*1.6*	*1.6*	*2.6*
Weekend	38.1	9.2	4.0	5.2	33.9	8.9	10.9	2.4	0.7	4.5
σ	*10.5*	*0.8*	*0.8*	*0.3*	*15.8*	*3.6*	*4.6*	*2.6*	*0.5*	*1.9*

Tab. 3 tunnel outside measurements- mean concentration for the investigated aerosol constituents..

Comparing the concentration pattern determined for the whole sampling period a similar trend for most of the compounds can be noticed (Fig. 4). The contribution of total carbon, black carbon and organic carbon to total suspended matter mass was nearly constant during the sampling period. Palladium concentrations run parallel to particle mass concentrations for most of the days, but some values e.g. the 4th of October do not fit into the pattern of other component concentrations. The behaviour of lead, copper, zinc and vanadium concentrations fit well to the trend found for particle mass and carbon parameter concentrations, only Nickel concentrations showed totally different behaviour compared to all other components.

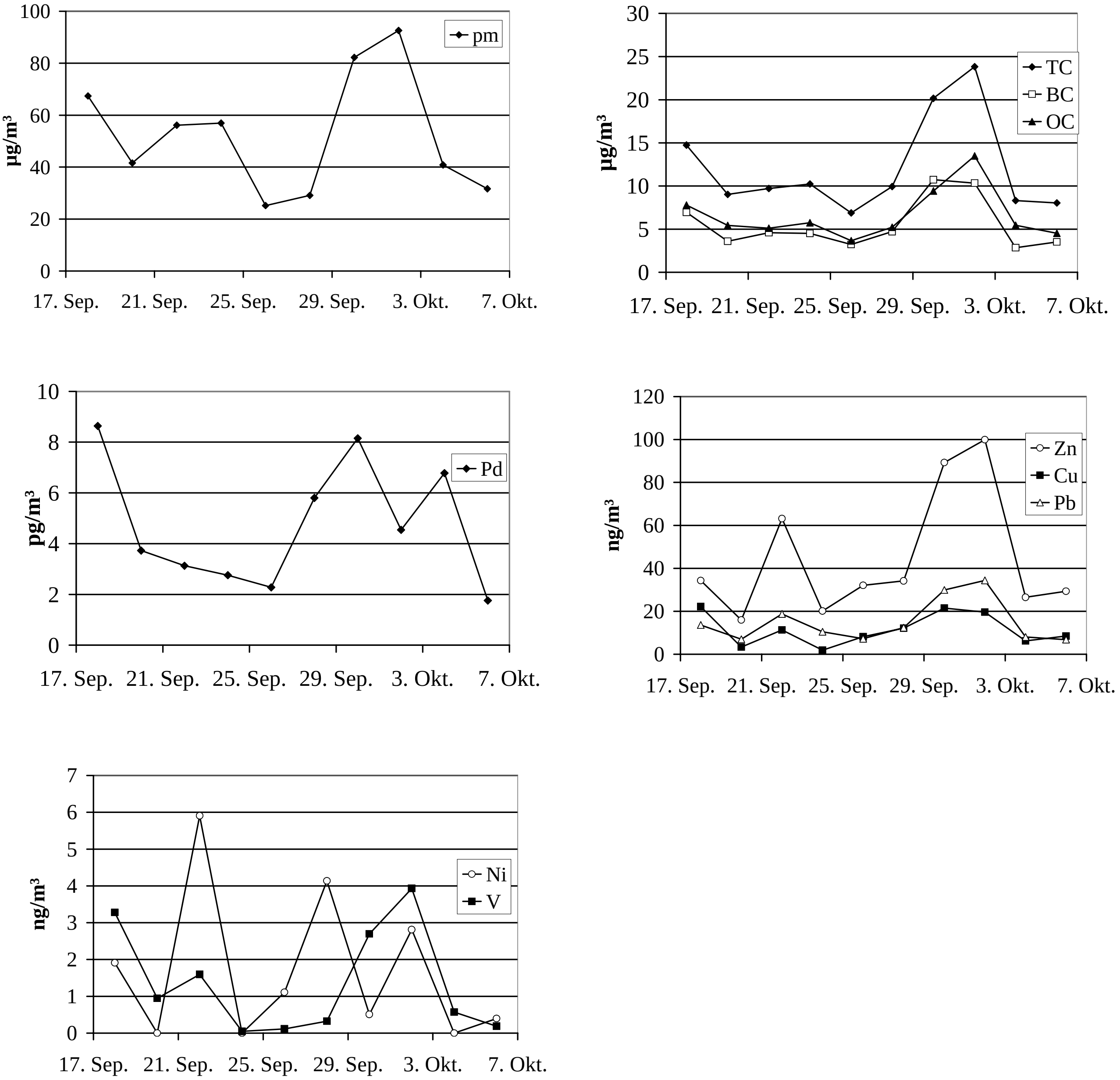


Fig. 4 Tunnel outside measurements- Time trend for individual component concentrations

Table 4 presents clearly the high correlation between most of the components hinted already by the charts. Component concentrations at the outside sampling site are influenced by several sources, mainly traffic pollution, power plants and space heating, since heavy industry is no important emitter in Vienna.

	TC	BC	OC	Zn	Cu	Pb	Ni	V	Pd
Pm	**0.86**	**0.81**	**0.83**	**0.62**	**0.46**	**0.78**	0.01	**0.78**	0.20
TC		**0.95**	**0.95**	**0.74**	**0.62**	**0.88**	0.01	**0.79**	0.23
BC			**0.82**	**0.76**	**0.70**	**0.88**	0.02	**0.74**	0.27
OC				**0.65**	**0.49**	**0.80**	0.02	**0.78**	0.18
Zn					**0.54**	**0.94**	0.15	**0.58**	0.07
Cu						**0.55**	0.11	**0.74**	**0.45**
Pb							0.12	**0.67**	0.13
Ni								0.06	0.00
V									0.32

Tab. 4 Tunnel outside concentrations-correlation table

Outside measurements are mostly influenced by metrological factors such as wind speed and wind direction which determine the dispersion and transport from the emission sources to the imission site. This observed high correlation between individual pollutant concentrations indicates that they have similar sources and that these emitters in the same direction relative to the sampling site. The total different behaviour of nickel concentrations compared to the concentrations of other compounds indicates that nickel concentrations were influenced by different sources.

Comparing the pollutant concentrations and the wind parameters a concurrence of the concentration peak between the 30th of September and the 3rd of October with lower wind speed and changing wind direction can be noticed (Fig. 4 and Fig. 5), thus the change of outside concentrations can be explained with the change of metrological conditions and a therefore different dilution of pollutants in the urban atmosphere.

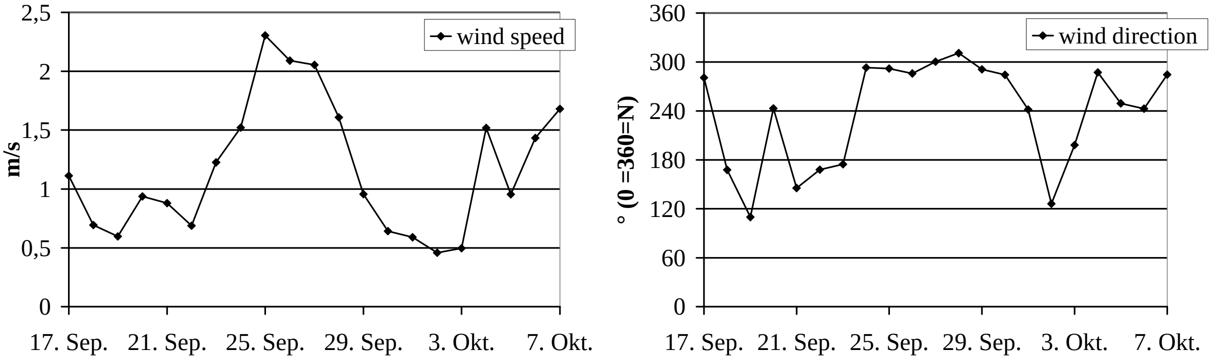


Fig. 5 Wind speed and wind direction during the sampling period

3.3 Tunnel inside measurements

During the tunnel inside measurements (20 samples) an average particle mass concentration of 127.5 µg m^{-3} was found. The mean value found for total carbon, black carbon and organic carbon was 76.0 µg m^{-3}; 49.7 µg m^{-3} and 26.3 µg m^{-3}. Average trace metal concentrations were 98.9 ng m^{-3}; 59.9 ng m^{-3} and 30.1 ng m^{-3} for zinc, lead and copper. The average concentrations found for nickel, vanadium and palladium were 2.4 ng m^{-3}, 2.0 ng m^{-3} and 16.0 pg m^{-3}. An overview of the results is presented in table 5. The Variation of all concentrations were much higher than analytical uncertainties. The observed concentrations accord well with other tunnel studies (Valiulis et al., 2002; Sternbeck et al., 2002) Similar to tunnel outside measurements concentration were lower during weekends (tab.5) and higher on workdays

	Pm	TC	BC	OC	Zn	Cu	Pb	Ni	V	Pd
	µg m^{-3}				ng m^{-3}					pg m^{-3}
Tunnel inside	127.6	76.0	49.7	26.3	98.9	59.9	30.1	2.4	2.0	16.0
σ	*26.9*	*11.0*	*7.0*	*4.8*	*53.4*	*35.0*	*15.4*	*3.2*	*2.1*	*4.3*
Workday	136.3	78.7	51.9	26.8	104.2	65.5	32.2	2.8	2.2	16.3
σ	*24.9*	*6.8*	*4.7*	*2.9*	*60.5*	*39.5*	*17.8*	*3.5*	*2.3*	*4.3*
Weekend	107.1	69.6	44.3	25.3	86.6	46.9	24.9	1.4	1.4	15.1
σ	*20.7*	*16.6*	*8.9*	*8.0*	*32.3*	*17.8*	*5.9*	*2.4*	*1.4*	*4.4*

Tab. 5 Tunnel inside measurements-mean concentrations for the investigates aerosol constituents

Compared to outside measurements, pollution levels inside the tunnel were fifty percent higher for nickel and vanadium, twice as high for zinc, lead and aerosol, three times higher for palladium, four to six time higher for copper, organic carbon and total carbon and nearly nine times higher for black carbon.

The amount of particulate matter made up by black carbon inside the tunnel was 40%, a relatively high amount compared to outside measurements, where black carbon contributed only 10 % to aerosol mass. This result is confirmed by other tunnel studies (Allen et al., 2001b ; Puxbaum et al., 1998), where also an increase of black carbon to the particulate matter mass was observed

In Fig 6 the time trends observed for different components are presented.. In addition Fig. 6 also includes the data for traffic and air velocity inside the tunnel.

Comparing the results a similar trend between air velocity and traffic density was observed, but this result was expected since the tunnel is designed to be ventilated through vehicular movement (fig. 6)

Related trends were also found for particulate mass, total carbon, black carbon and organic carbon, which is in good agreements with the pattern observed for traffic and air velocity.

Similar to the tunnel outside measurements comparable time trends were found for all trace metals except nickel. Changes of heavy metal concentrations inside the tunnel resemble changes of their concentration outside the tunnel, which is apparent for the concentration peak around the 2nd of October, which indicates the influence of pollution levels of incoming air entering the tunnel (fig. 4 and fig. 6).

The time trend found for palladium concentrations did neither fit to the trend observed for particulate matter and carbon parameters, nor to the time trend found for the trace metals. This indicated that the emission of palladium by traffic depends differently on the driving conditions.

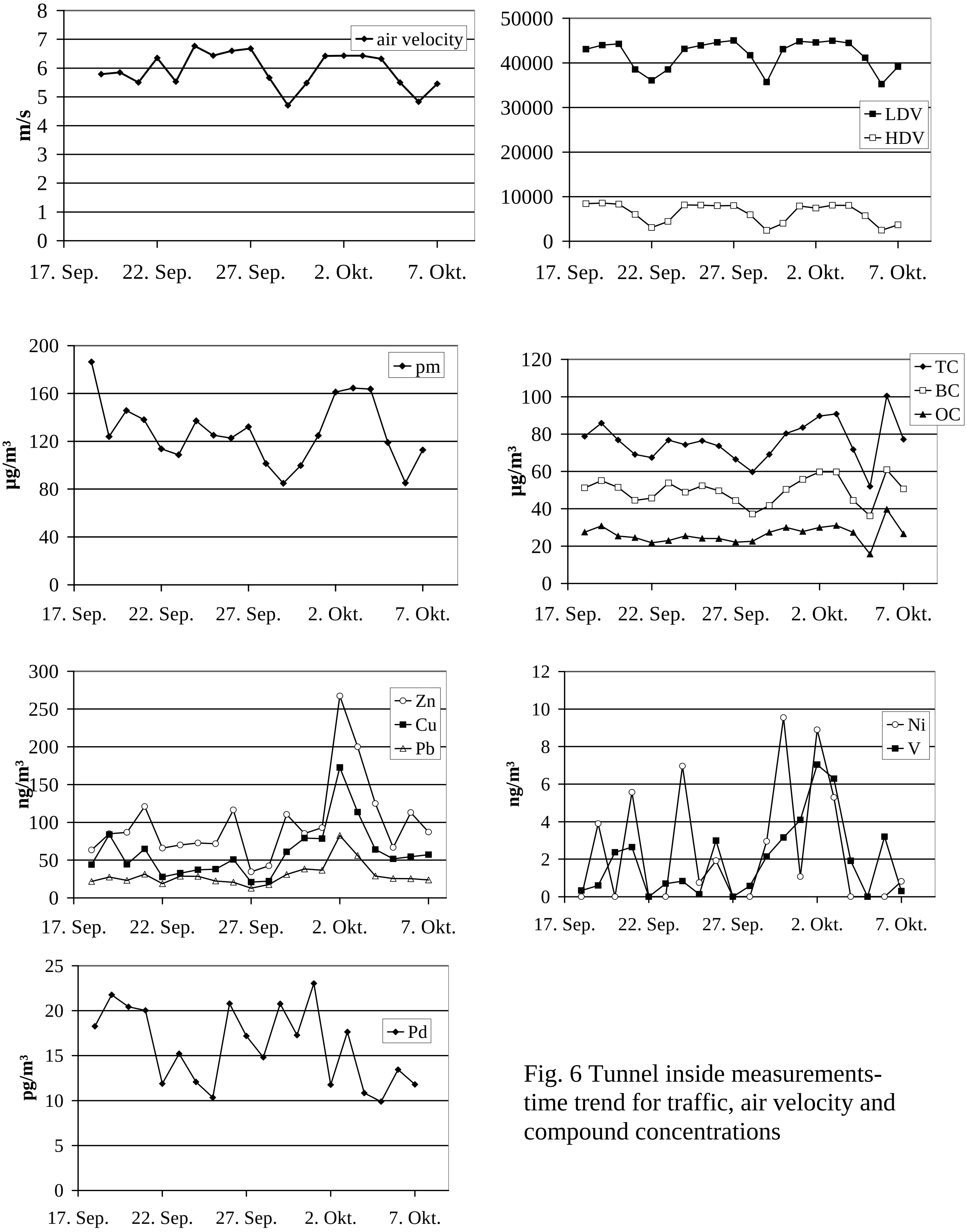


Fig. 6 Tunnel inside measurements-time trend for traffic, air velocity and compound concentrations

In table 6 the correlation coefficient for the tunnel inside concentrations is presented. As indicated already by fig. 6 high correlation coefficients between particulate matter, total carbon black carbon and organic carbon were obtained. High correlation coefficients were also received between zinc, lead, copper and vanadium. Surprising is the fact that heavy metal concentrations did not correlate with carbon or particulate mass concentrations, since traffic is their common source inside the tunnel and outside concentrations show a clear correlation, but due to the fact that these metals derive mainly from brake and tyre wear their emission depends more on the driving conditions than the emission of components like black carbon and particulate matter. As already indicated by fig. 6 palladium concentrations showed no correlation to any other component concentration.

	TC	BC	OC	Zn	Cu	Pb	Ni	V	Pd
Pm	**0.53**	**0.69**	0.21	0.40	0.46	0.44	0.18	0.48	0.01
TC		**0.91**	**0.82**	0.30	0.31	0.26	0.11	0.40	0.00
BC			**0.55**	0.30	0.31	0.28	0.09	0.37	0.01
OC				0.22	0.23	0.15	0.11	0.32	0.04
Zn					**0.83**	**0.83**	0.30	**0.78**	0.05
Cu						**0.90**	0.44	**0.71**	0.01
Pb							0.48	**0.72**	0.05
Ni								0.31	0.00
V									0.00

Tab. 6 Tunnel inside concentrations- correlation between tunnel inside concentrations

4. Determination of Emission Rates

4.1 Theoretical background

4.1.1 Emission factor for the total car fleet

The emission factor is defined as amount of compound emitted by a car per time , per driven distance or per mass fuel or carbon consumed.. The determination of the emission factor of traffic can either be done by tale pipe measurements or by field measurements at a site where other sources than traffic emissions can be excluded. Road tunnels with ventilation fulfil this criteria. If pollutant concentrations at the tunnel entrance and inside the tunnel are known as well as the amount of fresh air entering the tunnel per time, the amount of newly emitted pollutant could be easily calculated by multiplying the ventilation rate with the concentration difference between the entering air and the air inside the tunnel. To determine the amount of pollutant emitted per car and driven distance the total amount of generated pollutants has to be divided through the number of cars driven through the tunnel and the distance between the tunnel entrance and the sampling inside the tunnel. The following formula describes the mathematical connection of the parameters mentioned above.

$EF = \frac{(c_i - c_o)*V}{v*d}$	[kg] ^{1}[km]$^{-1}$
V= A*s	[m^3][sec]$^{-1}$
c_i…concentration inside the tunnel	[kg][m^3]$^{-1}$
co…concentration outside the tunnel	[kg][m^3]$^{-1}$
V…ventilation rate	[m^3][sec]$^{-1}$
v…number of vehicles passing through the tunnel	[sec]$^{-1}$
S…air speed in the tunnel	[m][sec]$^{-1}$
A…cross sectional area of the tunnel	[m^2]
d…distance from tunnel entrance to sampling site	[km]
EF…Emisison factor	[kg] [km]$^{-1}$

4.1.2. Calculation of separate Emission factors for LDV and HDV

The daily emission factor is a mixture of the emission factor of heavy duty vehicles and light duty vehicles. Because of their converse emission profiles it is assumed that heavy and light duty vehicles possess different emission factors. If the amount of heavy duty vehicles in the car fleet varies between the days than errors it is possible to calculate a separate emission factor for both vehicle groups.

The dependency of the mean emission factor on the traffic composition can be described as follows:

$Ef_{tot} = EF_{HDV} * h + Ef_{LDV} * l$

$l = 1-h$

$Ef_{tot} = Ef_{HDV} * h + Ef_{LDV} * (1-h)$

$Ef_{tot} = (Ef_{HDV} – Ef_{LDV}) * h + Ef_{LDV}$

The formula of the linear regression between the amount of heavy duty vehicles and the emission factor of the whole fleet leads to the calculation of the separated emission factors of heavy and light duty vehicles:

$y = k*x + d$

$d = Ef_{LDV}$

$y\ (h=1) = Ef_{HDV}$

Ef_{tot}	Emission factor of the total car fleet
Ef_{HDV}	Emission factor of heavy duty vehicles
Ef_{LDV}	Emission factor of light duty vehicles
h.	Relative amount of heavy duty vehicles in the car fleet
L	Relative amount of light duty vehicles in the car fleet

4.2 Results

4.2.1 Emission factor for the total car fleet:

The emission factors for particulate matter, total carbon,black carbon and organic carbon were in the range of several mg per vehicle and kilometre, the emission factors for all trace metals were generally three orders of magnitude lower in the µg per vehicle and kilometre range, and the emission factor for palladium was in the lower ng per vehicle and kilometer range. The average emission factors and their deviation is presented in table 7. The results show that nearly 60 % of vehicular particulate matter emissions by traffic are made up by black carbon, a percentage also found in dynamometer based studies (Williams et al., 1989). Zinc and copper emissions were nearly equal, lead emissions were approximately one third of emission of these two heavy metals.

	PM	TC	BC	OC	Zn	Cu	Pb	Ni	V	Pd
	mg v^{-1} km^{-1}				µg v^{-1} km^{-1}					ng v^{-1} km^{-1}
EF total *	46.8	39.7	27.5	12.2	34.2	30.2	9.5	1.8	1.0	7.1
σ	*17.5*	*6.7*	*4.3*	*3.0*	*29.9*	*20.2*	*6.7*	*2.1*	*0.7*	*2.9*
Workday	45.3	42.3	29.0	13.2	36.0	31.9	9.8	1.8	1.1	7.1
σ	*17.5*	*7.3*	*4.0*	*3.9*	*28.9*	*20.7*	*6.3*	*2.0*	*0.7*	*2.4*
Weekend	46.3	39.8	26.6	13.2	36.1	25.7	9.5	2.3	1.1	7.1
σ	*17.2*	*11.9*	*6.9*	*5.4*	*31.9*	*15.8*	*7.1*	*3.2*	*0.7*	*3.8*

Tab. 7 Mean values and standard deviation of calculated emission factors

* Values were calculated for the whole car fleet with an average amount of 12.6% HDV, 53% gasoline powered cars and 33% diesel powered cars

4.2.2 Separate emission factors for HDV and LDV

A statistical significant difference between workday and weekend values and therefore a dependence on the different fleet composition with an average amount of 14 % HDV on workdays and 8 % HDV during the weekend could only be observed for total carbon and black carbon (Tab. 7) For these two compounds a significant correlation to the amount of heavy duty vehicles in the fleet could be observed and the separate emission factors for heavy duty vehicles and light duty vehicles were calculated. Time trends and a comparison with values found in literature for single compounds are presented afterwards.

The following figure 7 shows the dependence of the emission factor of total carbon, black carbon and organic carbon on the relative amount of heavy duty vehicles in the car fleet over the whole sampling period.

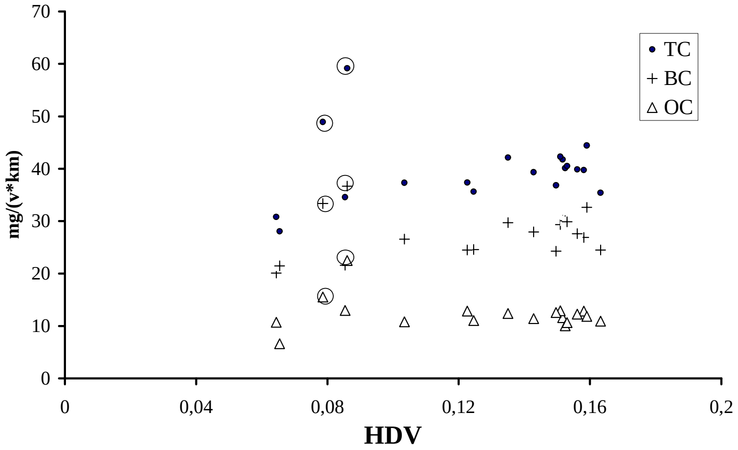


Fig. 7 Correlation between the relative amount of HDV and emission factors for carbon parameters

For all carbon fractions a clear correlation was observed, although some data points showed a clear deviation from the bend given by the whole data set. For the calculation of the regression the two values for the 21st September and the 6th October (marked with a circle, fig. 7) were excluded. On these days Emission factors for trace metals had also their maximum (chapter 4.3), so that an analytical error can be excluded.

Therefore it must be assumed that changes in the traffic flow and the average driving speed occurred on these days which caused a higher fuel consumption and a higher emission of elemental and total carbon. in the tunnel. The derived results including the statistical data are presented in fig. 8.

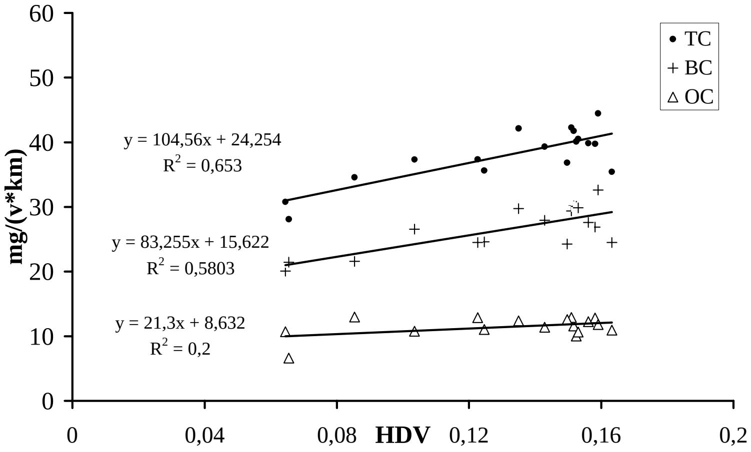


Fig. 8 Linear regressions and formula calculated for the dependence of Emission factors on the relative amount of heavy duty vehicles in the car fleet

It is apparent that heavy duty vehicles have a six times higher emission factor of all these components (tab.8), but this is not surprising since they also consume a lot more fuel per kilometer because of their heavyier weight compared to personal cars, and heavy duty vehicles are equipped 100 % with diesel engines in contrast to light duty vehicles, where diesel driven cars make up 38.5 % in Austria. Such high differences of the emission factor of these compounds was also found in literature (chapter 4.3).

mg/(v*km)	TC	BC	OC
HDV	128.8	98.9	29.9
LDV	24.3	15.6	8.6

Tab. 8 Calculated emission factors for light duty vehicles and heavy duty vehicles for total carbon, black carbon and organic carbon

4.3 Trends and comparison with literature:

4.3.1 Particulate matter:

The emission factor determined for particle matter was 46.8 mg v^{-1} km^{-1} with a relative standard deviation of 40 %. As can be seen in figure 9 no weekly trend could be observed which is not surprising since a big part of particulate matter derives from resuspended road dust, and this resuspension depends strongly on parameters like humidity or cleanness of the roadway (Sternbeck et al., 2002; Vardoulakis et al., 2003). During two periods (29th September to 1st October, and at the 6th October) the emission factor of particulate matter drops below the emission factor of total carbon, which is not plausible because total carbon mass is only a major part of particle mass, which leads to the assumption that on these days measured outside concentrations were not representative for air entering the tunnel due to different wind conditions. (see also chapter 3.2)

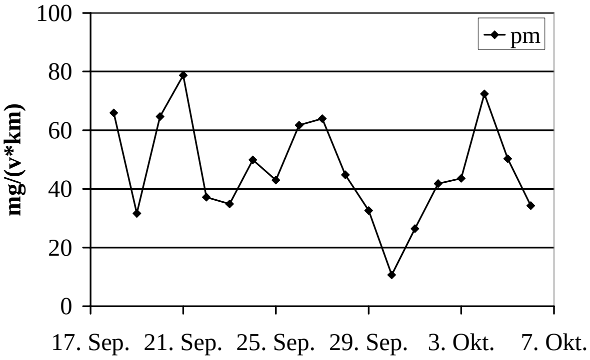


Fig. 9 Emission factors of particulate matter during the sampling period

The emission factor of particulate matter was comparable to the results derived from investigations in the Tauerntunnel (Puxbaum et al., 1998) and the Caldecott (Allen et al., 2002) tunnel. Dynamometer based values found by Williams et al. (1989) were much higher, the observed decreasein the present work can be explained the further technical development of diesel and gasoline engines since this dynamometer study was conducted. The emission factors for particulate matter found in recent tunnel studies performed in Göteborg (Sternberg et al., 2002) were much higher than the value found in the rpesent work, As mentioned before it ahs to be cosidered that the emission of particulate matter is strongly influenced by the resuspension of road dust , thus the observed difference is not surprising.

According to the estimation of particulate matter emissions by brake lining wear by Westerlund et al. 50 % of particulate matter emissions in the Kaisermühlen tunnel were made up by brake lining wear, which is not plausible because already 60 % of particulate matter emissions were made up by black carbon, but it can be assumed that not every particle formed by brake lining wear is distributed in the aerosol phase, for large particles a fast deposition through gravity can be expected. An overview of the emission factors described for particulate matter in literature is presented in table 9.

	Ef PM	Dimension	Vehicles
Present study	46,8 *17,5*	mg v^{-1} km^{-1}	12,6% HDV
Williams 1989 a (dynamometer)	228 *59*		PC diesel
	427 *190*		DV
	2090 *1750*		HDV
Williams 1989 b (dynamometer)	73 *46*		PC gasoline
+	381		Kaisermühlen car fleet
Sternbeck et al 2002 Göteborg	108 *58*		Tingstad tunnel (10,5% HDV)
	518 *324*		Lundby tunnel (13,7 % HDV)
Puxbaum et al. 1998	27		LDV
Tauerntunnel	469		HDV
+	83		Kaisermühlen car fleet
Westerlund et al. 2001	17		LDV
Brake lining wear estimates	84		HDV
+	26		Kaisermühlen car fleet
Allen et al 2001b * Caldecott tunnel pm10	4 *1*		LDV
	810 *56*		HDV
+	106		Kaisermühlen car fleet
	68 *24*	mg kg(C) $^{-1}$	LDV
	2262 *156*		HDV

Table 9 Values of emission factors found in Literature, standard deviations are in italic
+ Calculated for the average car fleet passing the Kaisermühlen tunnel containing 53% gasoline and 33% diesel light duty vehicles and 12,6 % heavy duty vehicles
*original data was mg kg(C)$^{-1}$, values for mg v^{-1} km^{-1} were recalculated using typical fuel economics presented in this paper

4.3.2 TC, BC and OC

The contribution of the black carbon emissions made up constantly two third of the amount of the emitted total carbon. For all three carboncaeous parameters a similar trend and a good correlation for the emisison factor was found (fig. 10). The correlation factor between individual carbon fractions is shown in table 10.

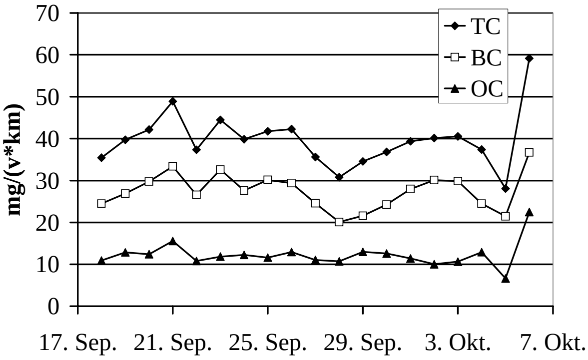


Fig 10 Trend of carbon emission rates during sampling period

	TC	BC
OC	0.74	0.39
BC	0.87	

Tab 10 Correlation between carbon emission rates

Comparing the results of the present studies with emission data for these parameters described in literature it is apparent that values found in the dynamometer based study by Williams et al. (1989) is much higher which can be explained with the age of this study and the development in engine technique especially for diesel engines sice this study was performed. Emission factors by Puxbaum et al. (1998) for the Tauerntunnel are comparable to emission factors determined for total carbon, black carbonand organic carbon in the present study, differences can be explained with the uncertainty of the calculation of the separate emission factors for light and heavy duty vehicles. Although the study in the Caldecott tunnel by Allen et al. (2001) was made recently, values were lower for light duty vehicles, which is no surprise because it is well known that diesel emgines emit more total and black carbon than spark ignition engines and the amount of diesel driven cars in the typical american fleet is much lower than in Austria (38 %). A compilation of the emission factor for total carbonand black carbon is presented in table 11.

	EF TC	EF BC	Dimension	Vehicles
Present study	24.3	15.6	mg v^{-1} km^{-1}	LDV
	128.8	98.9		HDV
	39.7 *6.7*	27.5 *4.3*		Kaisermühlen
Puxbaum et al. 1998	13			LDV
	339			HDV
	54			Kaisermühlen
Williams et al 1989 b		3 *1.7*		PC gasoline
Williams et al 1989 a		150 *40*		PC diesel
		60		LDV +
		102 *49*		DV
		690 *598*		HDV
		139		Kaisermühlen
Allen et al. 2001 b	5.8 *0.6*	2.6 *0.5*		LDV*
	713 *33*	458 *24*		HDV*
	90 *9.6*	40 *8*	mg $kg(C)^{-1}$	LDV
	1992 *62*	1278 *54*		HDV

Tab. 11 Comparison of carbon emission tares with values foun din Literature, Standard deviations are presented in italic letters

+ Calculated for the average LDV passing the Kaisermühlen tunnel containing 61.6% gasoline and 38.4% diesel vehicles
*original data was mg $kg(C)^{-1}$, values for mg v^{-1} km^{-1} were recalculated using typical fuel economics presented in this paper

4.3.3. Trace metals:

As mentioned before, the calculated emission factors of the trace metals zinc, copper lead, nickel and vanadium were in the µg per vehicle and kilometer range and variied significantly during the sampling period (Fig 11). The emission factors of vanadium and nickel were negative on some days due to higher tunnel outside than tunnel inside concentrations. For these days it must be assumed that concentrations found at the tunnel outside were not representative for concentrations at the tunnel entrance. Therefore nickel and vanadium emission factors found for these days were excluded from further calculations. No difference between workdays and weekend values and therefore no correlation with the relative amount of heavy traffic in the car fleet could be observed for the emisison factor of these elements.

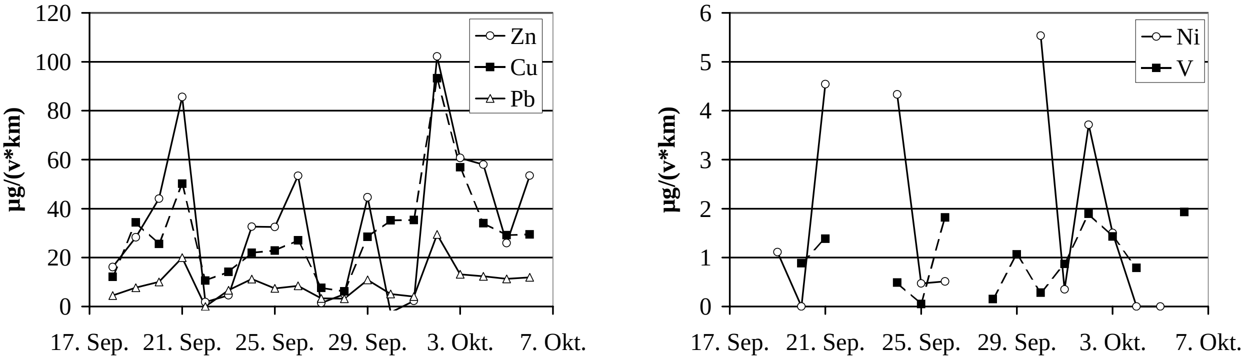


Fig. 11 Trend of emission factors of trace metals

Between the emission factor of the trace metals copper, zinc and lead , whose concentrations inside and outside the tunnel correlated also (chapter 3.2 and 3.3) A good correlation was found (tab 12).

	Zn	Cu
Pb	0,84	0,76
Cu	0,61	

Tab. 12 Correlation between copper, zinc and lead emission rates…

These correlations lead to the assumption that the emission of these elements is caused by the same processes or depend in the same way on changings of driving conditions.

Similar to the results for particulate matter and the carbonaceous fractions a comparsion of the results derived from the Kaisermühlen tunnel study with literature data was performed (Tab.13)

	Zn	Cu	Pb	Ni	V	Dimension	characteristics
Present study	34.2 *29.9*	30.2 *20.2*	9.5 *6.7*	1.8 *2.1*	1.0 *0.7*	µg v^{-1} km^{-1}	12.6 % HDV
Sternbeck et al. 2002 Göteborg	205 *87.5*	172 *37*	36.9 *7.7*				Tingstad tunnel 10.5% HDV
	239 *25*	147 *32*	35.1 *13.6*				Lundby tunnel 13.7% HDV
Valiulis et al. 2002 Vilnius	114 *23*	98 *12*	19 *3*				7 % HDV >2.5 mm
	92 *26*	61 *9*	35 *6*				< 2.5 µm
Puxbaum et al. 1998 Tauerntunnel	31	111	72	1			LDV
	448	5	161	134			HDV
	83	97	83	18			Kaisermühlen +
Westerlund 2001 Brake wear estimates	291	1398	207	2			LDV
	756	756	43	10			HDV
	350	1317	187	3			Kaisermühlen+
Allen et al. 2001 b Caldecott tunnel	0				0.0003		LDV*
	13.6				0.0057		HDV*
	1.7				0.0010		Kaisermühlen +
	-0.2 *1.6*				0.0046 *0.00061*	µg kg(C)$^{-1}$	LDV
	38 *10*				0.0158 *0.004*		HDV

Tab. 13 Comparison of emission rates of trace metals found in literature, standard deviations are in italic

+ Calculated for the average car fleet passing the Kaisermühlen tunnel containing 53% gasoline and 33% diesel light duty vehicles and 12.6 % heavy duty vehicles

*original data was mg/kg C, values for mg/(v*km) were recalculated using typical fuel economics presented in this paper

Apparent in this overview of the emission factors. is the fact, that the emission values of these trace metals variied significantly between all studies, only the emission factors found in the Tauerntunnel by Puxbaum et al (1989) were in the range of the emission values found in the present study. The estimates of the emission factors of these trace metals by break lining wear by Westerlund et al. (2001) is again much higher than the emission factor found in the Kaisermühlen tunnel, but as mentioned in the discussion of the results for particulate matter emission it cannot be assumed that all particles emitted by brake lining wear are in the size range which contributes to atmospheric aerosol (chapter 4.3.1).

However, the high emission value calculated for brake wear estimates leads to the assumption that brake lining wear is the biggest contributor to the emission of the three trace metals zinc, copper and lead, which also explaines the high correlation found between the concentrations and the emission factors of these elements. The lower emission factors in the Kaisermühlentunnel compared to the tunnel studies performed by Sternbeck et al. (2002) and Valiulis et al. (2002) can be explained by the fact that the traffic density in the Kaisermühlen tunnel is usually low enough for a rare need of braking maneuvers inside the tunnel, the even lower emission factor for zinc and vanadium found by Allen et al. (2001 b) in the Caldecott tunnel confirms this assumption, since theCaldecott tunnel is a highway tunnel with the same amount of lanes and a lower traffic density.

4.3.4 Palladium

The mean emission factor found for palladium was 7.1 ng v^{-1} km^{-1} and showed lower variation than the emission factor of other trace metals.Similar to particulate matter and all trace metals no weekly trend was observed for the emission factor of palladium (Fig 12), even if the palladium emission caused by light duty vehicles and heavy duty vehicles are known to be significantly different, but it must be assumed that uncertainties in sample preparation and detection were too high to observe a correlation with the relative amount of heavy duty vehicles.

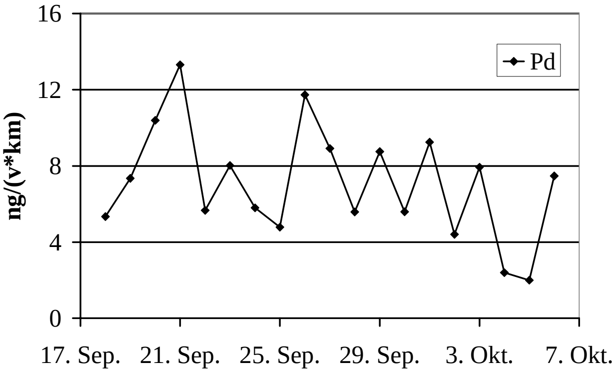


Fig. 12 Trend of Palladium emission rates during the sampling period

The presented emission factor for palladium is the first value which was determined under real world conditions, thus it is not possible to compere the result with literature data from other field investigations, until now only bench test studies were performed.The emission factor found in the present study accords well with the emission factors found by dynamometer based studies (Moldovan et al., 2002), which are shown in table 14. Their measurements revealed that the emission of palladium by the catalyst decreases with the age of the catalyst and that even \`Pt only\` labbeled diesel catalysts emitted palladium. Because of the high variation of the emission of palladium in dynamometer measurements and the fact that platin emission rates of catalysts depend on driving conditions such as veloctiy (Artelt et al., 1998) it must be assumed that these driving conditions also have an influence on the emission of palladium.

	EF Pd (ng v^{-1} km^{-1})	
Present work *σ*	7.1 *2.9*	Total car fleet
σ	13.4 *5.5*	Gasoline driven cars
Moldovan et al. 2002 *range* Dynamometer test of single catalyst equipped cars	54.2 *22.0-108.0*	Pt/Pd/Rh 0km
	7.9 *1.9-14*	30000-80000 km
	41.6 *15.5-132.1*	Pd/Rd 0km
	7.7 *1.9-21.5*	30000-80000km
	28.1 *4.2-84.4*	Diesel Pt only 1 0km
	37.3 *4.0-110.4*	30000-80000
		Diesel Pt only 2 0km
	58.4 *2.6-285.6*	30000-80000km

Tab. 14 Emission rates of palladium found in Literature, standard deviation respectively ranges are presented in italic

4.4 Summary:

Generally emission factors varied during the investigated period, and only the emission factor of total carbon, black carbon and organic carbon correlated to the amount of heavy traffic in the car fleet. Emission factors accorded generally well with values found in literature. Correlations remaining after the calculation of the emission factor indicate a similar dependency of the emissions on traffic composition, driving mode and average driving velocity.

The daily trend of the emission factors showed high correlation between compounds with similar dependencies on traffic fleet composition and driving conditions such as total carbon, black carbon, organic carbon and copper, zinc, lead (Tab. 15). Generally correlation values for emission factors were lower than correlation values found for concentrations, but this can be explained by the fact that correlation caused by traffic density, dilution of emitted pollutants with fresh air entering the tunnel and changing pollution levels outside the tunnel disappears during the calculation of the emission factor.

	TC	BC	OC	Zn	Cu	Pb	Ni	V	Pd
Pm	0.00	0.00	0.00	0.16	0.00	0.05	0.06	0.04	0.04
TC		**0.87**	**0.74**	0.17	0.05	0.09	0.08	0.34	0.22
BC			0.39	0.20	0.11	0.14	0.04	0.36	0.20
OC				0.07	0.00	0.01	0.11	0.17	0.15
Zn					**0.61**	**0.84**	0.02	**0.53**	0.03
Cu						**0.76**	0.13	0.35	0.00
Pb							0.13	0.39	0.00
Ni								0.00	0.01
V									0.13

Tab. 15 Correlation of emission factors of all measured components

5. Application of Palladium as tracer

5.1 Description of the tracer model:

As described in the introduction (chapter 1) the tracer model is based on the assumption, that the component used as tracer is only emitted by one source, and the emission ratio between this tracer and the pollution is known, it is possible to calculate the amount of pollutants caused by this source by simply multiplying the tracer concentration with the emission ratios (2) and to calculate the relative contribution to imission from this source (3). Emission ratios for traffic can be calculated from Emission factors obtained in tunnel studies and dynamometer based studies (1).

$$r_{it,s} = Ef_{i,s}/Ef_{t,s} \qquad (1)$$

$$c_{i,s} = c_{t,s} * r_{i,t} \qquad [kg][m]^{-3} \qquad (2)$$

$$a_s = c_{i,s}/c_i \qquad (3)$$

$r_{it,s}$……………………..	Emission ratio between pollutant i and tracer t from source s	
$Ef_{i,s}$…………………...	Emission factor of pollutant i from source s	$[kg][km]^{-1}$
$Ef_{t,s}$…………………...	Emission factor of tracer t from source s	$[kg][km]^{-1}$
$c_{i,s}$…………………….	Concentration of pollutant I caused by source s	$[kg][m]^{-3}$
$c_{t,s}$…………………….	Concentration of tracer t from source s	$[kg][m]^{-3}$
a_i……………………...	Relative amount of pollutant concentration i caused by source s	
c_i……………………...	Concentration of pollutant I at imission site	$[kg][m]^{-3}$

Scatter plots between the emission factor of palladium and individual compounds showed an even distribution of values over the whole sampling period, so that average emission factors could be used for the calculation of the emission ratios. In Fig. 13 scatter plots of particulate matter and carbonaceous fractions with palladium are presented.

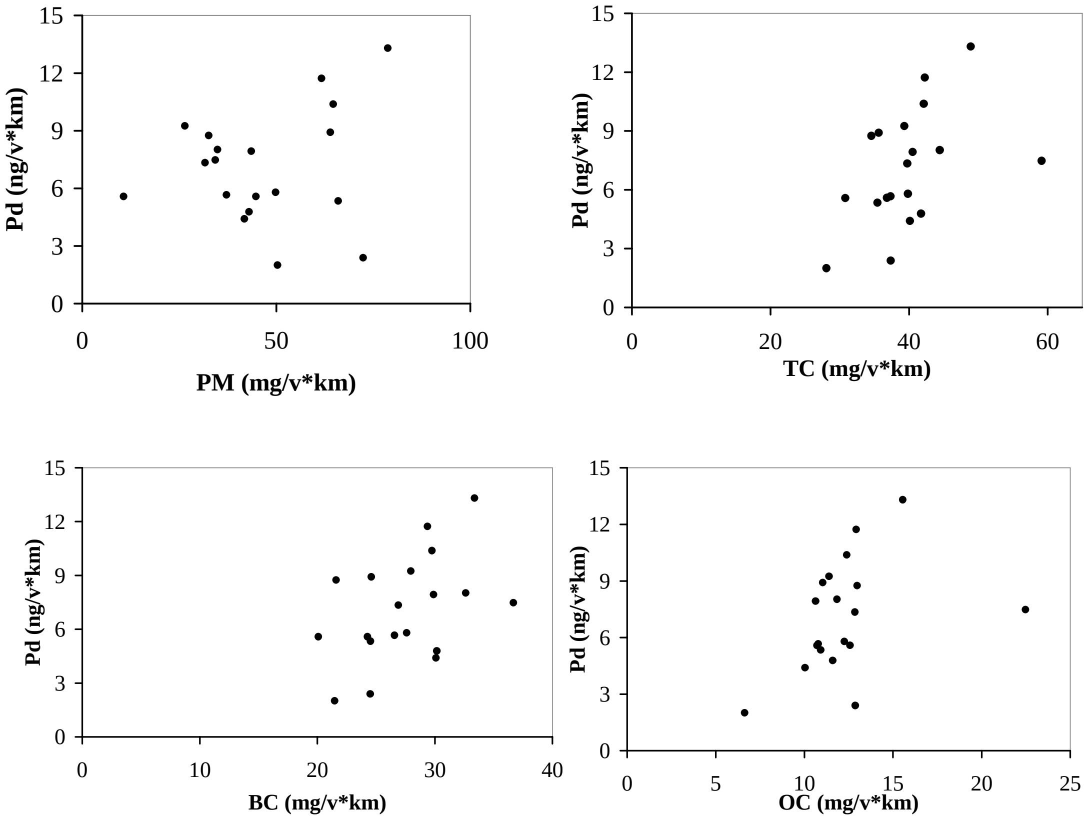


Fig. 13 Emission factor - scatter plot between main components and palladium

Emission ratios between palladium and other components were calculated from Emission factors described in table 16. Presented mean values for the whole sampling period were calculated for the whole car fleet with an average amount of 12.6 % HDV, 53 % gasoline powered cars and 33 % diesel powered cars

	Pm	TC	BC	Oc	Zn	Cu	Pb	Ni	V	Pd
EF *	mg v^{-1} km^{-1}				µg v^{-1} km^{-1}					ng v^{-1} km^{-1}
	46.8	39.7	27.5	12.2	34.2	30.2	9.5	1.8	1.0	7.1
σ	*17.5*	*6.7*	*4.3*	*3.0*	*29.9*	*20.2*	*6.7*	*2.1*	*0.7*	*2.9*
Ratios	mg ng^{-1}				µg ng^{-1}					
	6.6	5.6	3.9	1.7	4.8	4.3	1.3	0.25	0.14	
σ	*3.7*	*2.5*	*1.7*	*0.8*	*4.6*	*3.3*	*1.1*	*0.31*	*0.11*	

Tab. 16 Emission factors and calculated emission ratios to palladium for the investigated compounds.

* Values were calculated for the whole car fleet with an average amount of 12.6% HDV, 53% gasoline powered cars and 33% diesel powered cars

5.2 TU Vienna and Oberwart

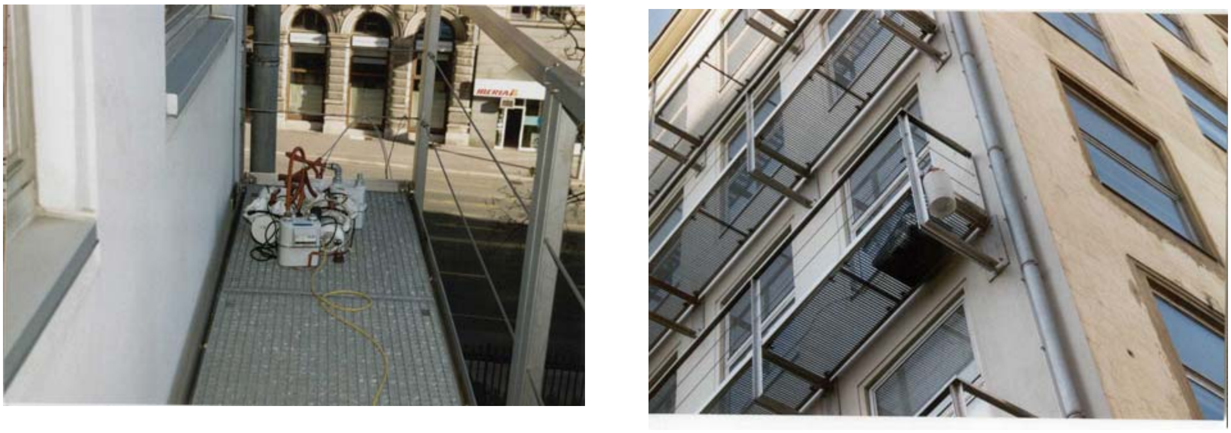
5.2.1 Description of the sampling sites

To verify the applicability of palladium as tracer for traffic emissions a sampling campaign at a typical urban site in Vienna was carried out in October 2002, and to get additional values for regional background concentrations, measurements were conducted in Oberwart in November 2002. Fig. 14 illustrates the geographical location of Oberwart and Vienna.

Fig. 14: Geographical location of Oberwart and Vienna:

<u>Vienna</u>:

The TU Vienna was chosen as site for urban measurements. It lies at the border of the inner city of Vienna near the Secession and the Mariahilfer Straße and is surrounded by several major roads. Representative city air samples were taken at the fire escape of the IAC-building at the 4th floor using open face filter heads, which were protected from rain by a shelter. Similar to the study performed in the Kaisermühlen tunnel cellulose ester filters were used for the determination of particulate matter and palladium and quartz fibre filters were used for the analysis of total carbon, black carbon, organic carbon and the trace metals zinc, copper, lead, vanadium and cadmium. Samples were taken at the 23, 24, 25 and the 28, 29 and 30th of October.



Pic. 3 and 4 TU Vienna measurement site

Oberwart:

Oberwart lies in the Burgenland near the Hungarian border, has about 8000 inhabitants and possesses no heavy industry. The sampling site was situated on a hill at the city border. The open face sampling heads were fixed under a polyethylene bucket at 2 m height at the side wall of a tool shed. Samples were taken from November the 3rd to November the 9th. In Fig 15 a city plan of Oberwart and the location of the sampling site is presented.

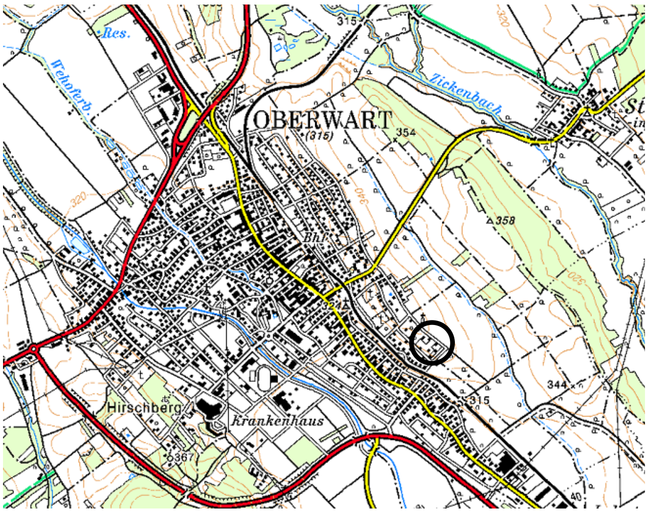
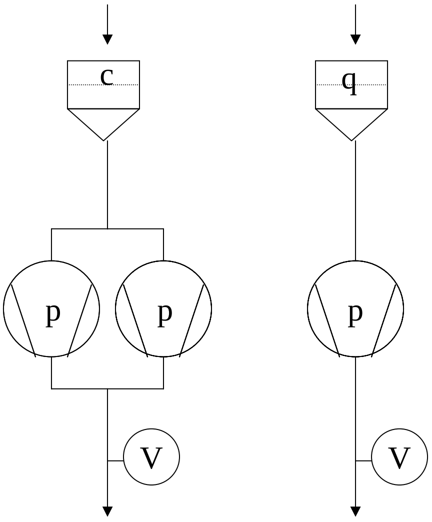


Fig. 15 City plan of Oberwart and location of the sampling site

Pic. 5 Oberwart sampling site

5.2.2 Sampling and sample treatment

For the Oberwart and Vienna measurements two membrane pumps were combined for one cellulose ester (Pall-Metricel Membrane filter 47mm 0.8 µm) sampling line obtaining a total flow of 42 l min^{-1}. The sampling line for quartz fibre filters (Pallflex membrane filter-Tissuequarz 2500QAT-UP) was composed of one membrane pump with a total flow of 35 l min^{-1}. A schematic illustration of the used set-up for sample collection is shown in fig. 16. On both sites sampling intervals were taken for 24 h, the filters were changed between 8 and 9 o clock in the morning.



q… Quarz Tissue filter
c… Cellulose ester filter
p…diaphragm pump
V... volume flow measurement

Fig. 16 Scheme of the sampling lines

Samples were treated and analysed alike tunnel inside and tunnel outside samples as described in chapter 2.2.

5.2.3 Results

TU Vienna

The average particulate matter concentration at the TU Vienna was 50 µg m^{-3}, nearly equal to the tunnel outside measurements and therefore also comparable to literature (chapter 3.1) One third of particulate matter mass was made up by total carbon. Total carbon itself consisted of equal parts of black carbon and organic carbon, similar to the tunnel outside measurements (chapter 3.2). Trace metal concentrations were in the medium ranged from the medium ng per m³ range to the low ng m^{-3} range and were also comparable to tunnel outside measurements and literature, as was the amount of black carbon contributing to particle mass. Pd levels of 8.1 pg m^{-3} were higher compared to the tunnel outside measurements. The mean results for the six aerosol samples from Vienna are presented in table 17. Standard deviations of concentrations were all higher than the calculated uncertainty of sampling and sample treatment (chapter 2.3)

	Pm	TC	BC	Oc	Zn	Cu	Pb	Ni	V	Pd
	µg m^{-3}				ng m^{-3}					pg m^{-3}
TU Vienna	50.0	16.3	8.1	8.2	49.0	20.6	15.8	4.0	1.6	8.1
σ	*8.7*	*2.7*	*1.6*	*1.4*	*35.8*	*12.1*	*10.1*	*2.6*	*1.1*	*5.1*

Tab. 17 Average measured concentrations of the TU Vienna sampling site

In fig. 17 observed time trends for the investigated aerosol constituents are depicted. The concentration of total carbon, black carbon and organic carbon concentrations followed all the same trend as particulate matter concentrations

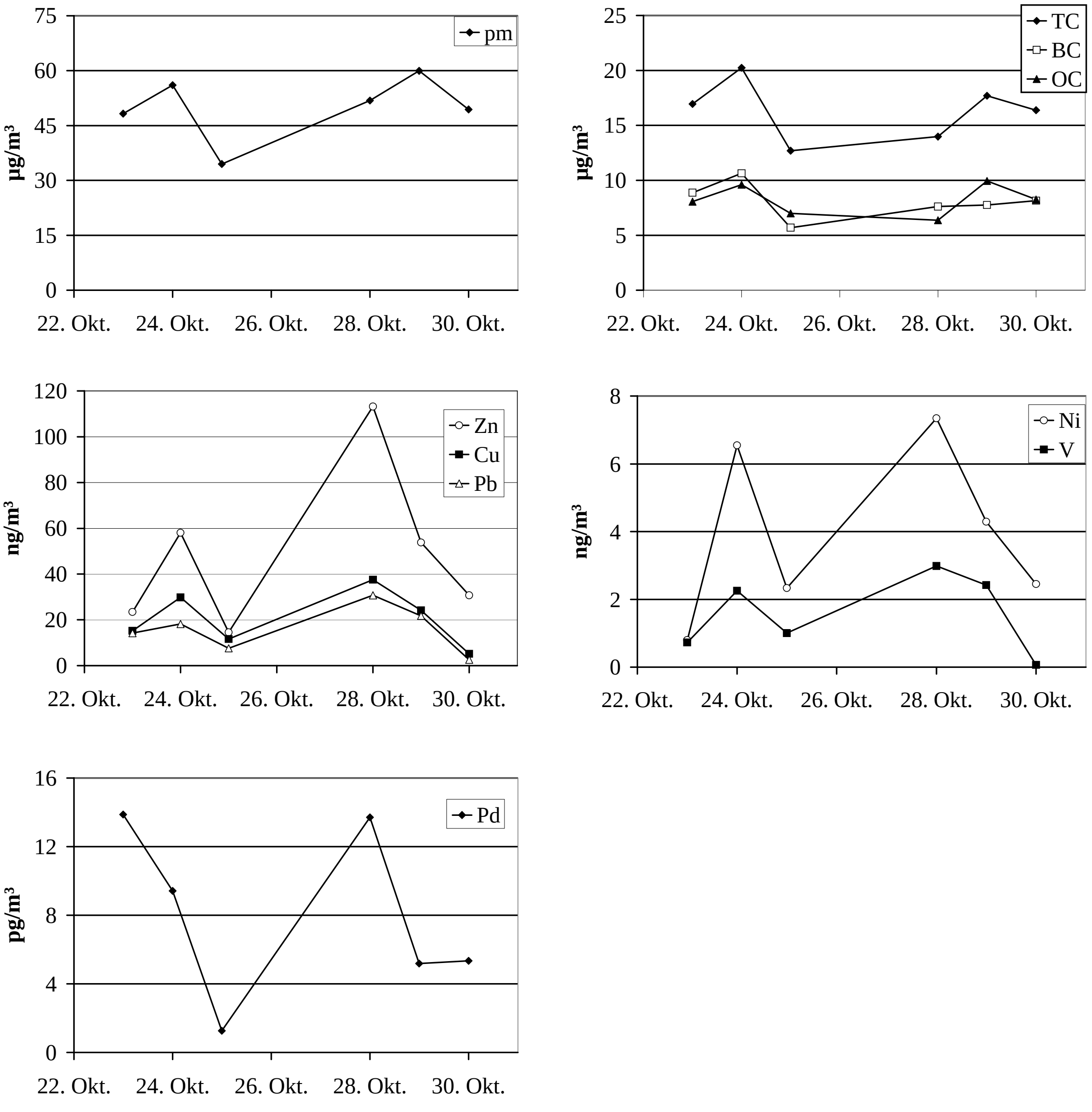


Fig. 17 Trend of component concentrations for the TU Vienna campaign

Trace metal concentrations, and different to the sampling site at the Kaisermühlen tunnel, even nickel concentrations showed good correlations (Tab. 18), even palladium concentrations - except the value received for the 23rd October – correlated good to other trace metal concentrations.

	TC	BC	OC	Zn	Cu	Pb	Ni	V	Pd	Pd *
Pm	**0.56**	0.43	0.46	0.27	0.28	0.29	0.25	0.28	0.15	0.29
TC		**0.82**	**0.76**	0.00	0.03	0.01	0.03	0.02	0.06	0.04
BC			0.34	0.03	0.10	0.03	0.09	0.02	0.29	0.26
OC				0.04	0.00	0.00	0.00	0.01	0.03	0.03
Zn					**0.78**	**0.76**	**0.78**	**0.69**	0.30	**0.90**
Cu						**0.91**	**0.78**	**0.92**	0.30	**0.68**
Pb							**0.56**	**0.88**	0.36	**0.59**
Ni								**0.75**	0.08	**0.85**
V									0.11	0.47

Tab 18 Correlation between measured components

* first day excluded from calculation

The lacking correlation between carbon parameters and trace metals and the different behaviour of nickel compared to the tunnel outside measurements can be explained with a stronger interference from pollutants deriving from space heating which was caused by lower temperatures and the start of the heating period in Vienna.

Oberwart:

In Oberwart (seven samples) average particulate matter concentrations were 29 µg m^{-3}, which was nearly one half of the concentrations found at the TU Vienna and had a higher variation (Tab. 19). Palladium concentrations were lower than the detection limit for the whole sampling period, and in contrast to Vienna significant concentrations of cadmium were determined. (Tab. 19) The reason for detectable cadmium levels was probably the observed use of brown coal for space heating by a household near the sampling site.

	Pm	TC	BC	Oc	Zn	Cu	Pb	Cd	Ni	V	Pd
	µg m^{-3}				ng m^{-3}						pg m^{-3}
Average	29.2	10.2	4.1	6.1	24.1	3.9	9.8	0.14	1.26	0.45	b.d.
σ	*10.9*	*4.7*	*1.7*	*3.0*	*17.2*	*2.4*	*3.9*	*0.19*	*1.03*	*0.40*	
TU Vienna	50.0	16.3	8.1	8.2	49.0	20.6	15.8	b.d.	4.0	1.6	8.1
σ	*8.7*	*2.7*	*1.6*	*1.4*	*35.8*	*12.1*	*10.1*		*2.6*	*1.1*	*5.1*

Tab 19 Concentration of measured components in Oberwart

b.d.…below detection limit

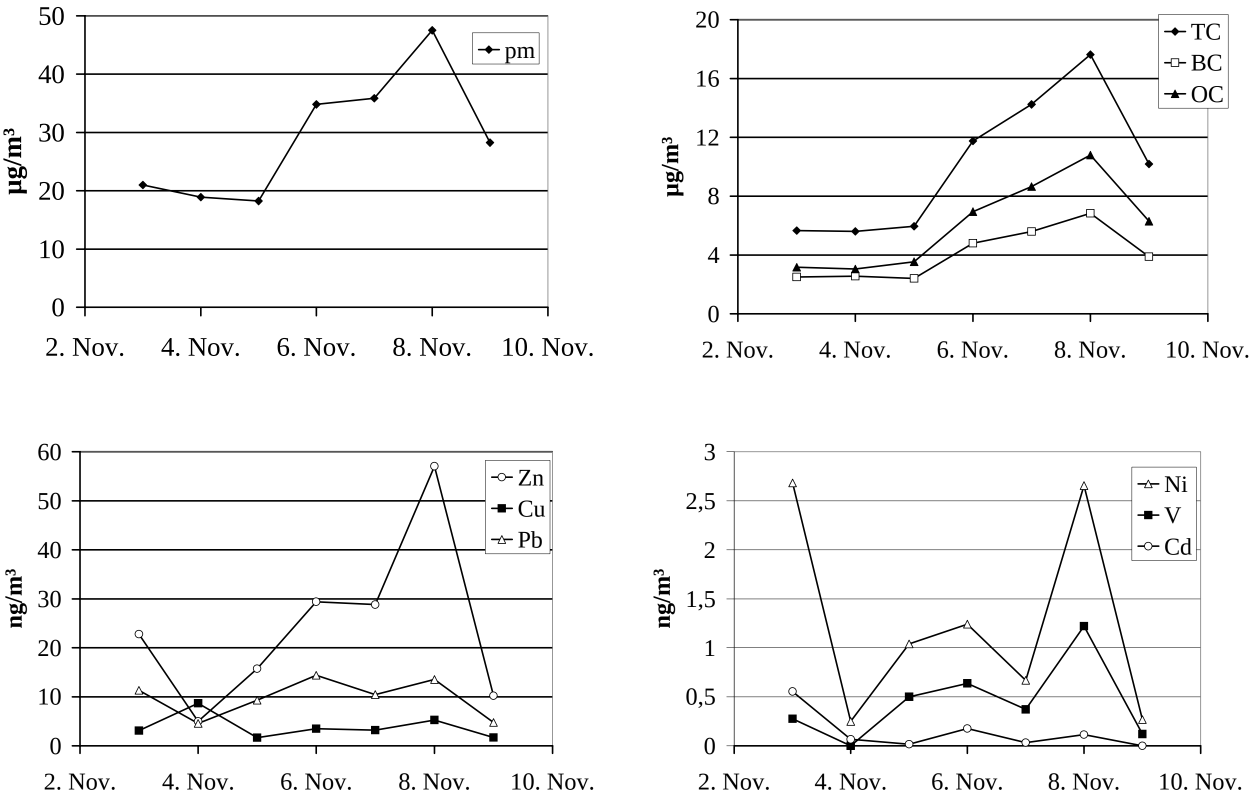


Fig. 18 Concentration trends at the Oberwart sampling site

Low concentrations of particulate matter, total carbon and black carbon in the first three days can be explained with a strong north-west wind which led to a better dilution of the pollutants. The high correlation between these compounds with zinc and vanadium indicates, that the concentrations of these compounds were influenced by the same sources (Tab. 20). Different to the other sampling sites copper, lead and zinc concentrations showed no correlation, which leads to the assumption that traffic was not the only source influencing concentration levels at the Oberwart sampling site.

The following correlation table illustrates the high correlations between the amount of particulate matter, total carbon, black carbon, organic carbon, zinc and vanadium in ambient air.

	TC	BC	OC	Zn	Cu	Pb	Cd	Ni	V
Pm	**0.97**	**0.98**	**0.96**	**0.77**	0.00	0.35	0.03	0.12	**0.61**
TC		**0.99**	**1.00**	**0.68**	0.00	0.27	0.08	0.06	**0.53**
BC			**0.99**	**0.70**	0.00	0.30	0.07	0.07	**0.54**
OC				**0.67**	0.00	0.25	0.09	0.05	**0.53**
Zn					0.00	**0.65**	0.02	**0.52**	**0.88**
Cu						0.04	0.00	0.00	0.00
Pb							0.15	**0.51**	**0.62**
Cd								**0.51**	0.00
Ni									0.43

Tab. 20 Correlations of measured component at the Oberwart sampling site

5.3 Application of the tracer model

To proof the usability of palladium as tracer component for automotive aerosol emissions the tracer model obtained in the tunnel measurements was applied to the aerosol measurements conducted at the TU Vienna. It was the aim of this application to receive the relative contribution of traffic to pollution concentrations in urban air in Vienna. The tracer model could not be applied to Oberwart measurements due to palladium concentrations below the detection limit.

Using the determined palladium concentrations and the ratios for the emission factors described in table 16 the expected concentrations for particulate matter, total carbon, black carbon, organic carbon and the trace metals were calculated. And compared to the results derived from the sample analysis. An overview of calculated ($c_{i,t}$) and analysed (c_i) concentrations is presented in table 21.

	Pm	TC	BC	OC	Zn	Cu	Pb	Ni	V	Pd =ct
	µg/m³				ng/m³					pg/m³
c_i	50.0	16.3	8.1	8.2	49.0	20.6	15.8	4.0	1.6	8.1
$c_{i,t}$	53.7	45.5	31.5	14.0	39.3	34.7	10.9	2.1	1.2	
σ	*30.1*	*20.3*	*13.8*	*6.5*	*37.4*	*26.8*	*8.9*	*2.5*	*0.9*	
r(%)	107	279	388	171	80	169	69	53	73	
σ	*60*	*125*	*170*	*79*	*76*	*130*	*56*	*64*	*57*	

Tab. 21 Concentrations at the TU Vienna (ci), estimation of the amount of concentrations caused by traffic (ci,t) with the tracer model, and the relative amount of pollutant concentration caused by traffic (r).

As can be seen in table 21, the calculated amount of particulate matter deriving from traffic significantly exceeds the analysed amount of particulate matter. The highest mismatch between estimated and measured concentrations was found for black carbon, total carbon and organic carbon. Only for the trace metals except cooper plausible results were obtained.

This mismatch between concentrations extrapolated with the tracer model can be explained with different emission ratios between palladium and other pollutants from traffic at the sampling site in downtown Vienna compared to the tunnel study. Dynamometer based studies (Modlovan et al. 2002) found, that the emission of palladium by catalyst is dependent on engine running conditions and the average driving velocity. The driving conditions in the Kaisermühlen tunnel is mainly free cruising at 80 km h^{-1}, whereas the TU Vienna is surrounded by traffic light equipped crossings which leads to a stop and go driving mode. Further it must be considered that other influences which are not included in this dynamometer studies, like road surface roughness, can have an influence on the emission of palladium containing particles from the catalyst. Further studies (Ericsson 2001) found 16 independent driving pattern factors which influence fuel consumption and exhaust emission factors for hydrocarbons and NO_x, so it can be said that generally all emission factors of traffic are heavily influenced by the driving speed, and that the driving mode in the Kaisermühlen and in the inner city of Vienna are too different to use the same emission ratios for a tracer based estimation of pollution caused by traffic.

6. Summary

Air pollutants are emitted by many sources, such as traffic, industry, power plants and municipal waste incineration. It is difficult to determine the contribution of different sources to total pollution concentrations. A straight forward method to determine the amount of pollutants deriving from one source is the sue of tracer models. A tracer component is a compound whose emission is dominated by one source so that the contribution from other sources can be neglected. If the emission ratio between the tracer component and other pollutants is known, it is then possible to calculate the amount of pollutants deriving from this source by the determination of the tracer concentration.

In future traffic will be the focus for environmental studies and considerations, because it is the only major pollution source in the developed world with increasing activity, thus it is necessary to determine the contribution of traffic emissions to the ambient pollutant concentrations.

With the introduction of the three way catalyst in the late 80s it was possible to reduce the emission of hydrocarbons and NOx to less than 10 %, but the three way catalyst added platinum group elements to aerosol emissions from traffic. These elements are known to have no other source of comparable magnitude, so the question arises if these metals can be used as tracer for pollution caused by traffic.

To investigate the ability of palladium to serve as tracer for traffic emissions a tunnel study was performed. To determine emission factors representative aerosol samples for tunnel outside and tunnel inside concentrations were taken during a three week period from the 17th September to the 7th October in the Kaisermühlen tunnel. The obtained sample set was analysed for particulate matter, total carbon, black carbon, organic carbon, zinc, copper, lead, nickel, vanadium, cadmium and palladium concentrations. For tunnel outside concentrations of total carbon, black carbon, particle mass and all trace metals except cadmium and nickel a good correlation was found, an indication that these compounds derive from similar sources. The determined Concentrations were comparable to literature data.

In the tunnel increased concentrations for all compounds were observed on weekdays, whereas reduced levels were determined for weekend samples. Comparing the results for tunnel inside and outside measurements, increased concentrations of the investigated aerosol constituents were measured. For the aerosol mass and the trace metals except copper an averaged increase of the concentration by a factor of 2-3 was found, whereas for copper, total carbon and organic carbon six times higher concentrations were observed, the greatest difference occurred for black carbon with averaged nine times higher concentrations inside the tunnel.

Using these results and the data for traffic density and air velocity inside the tunnel, emission factors were calculated.. For particulate matter an emission factor of 46.8 mg km^{-1} car^{-1} was obtained. This value was not comparable to other literature data, which could be explained with the influence of resuspension to particulate matter concentrations. The emission factor of total carbon was 39.7 mg km^{-1} car^{-1}, with a contribution of 27.5 mg km^{-1} car^{-1} from black carbon and 12.2 mg km^{-1} car^{-1} from organic carbon. The emission factor of the carbon fractions were more or less stable during the sampling period and comparable to literature data, their observed high correlation with the amount of heavy duty vehicles in the car fleet enabled the calculation of separate emission factors for heavy duty vehicles and light duty vehicles, with a six times higher emission factor for heavy duty vehicles for all three carbon components. Average emission factors of 34.2, 30.2, 9.5, 1.8 and 1.0 µg km^{-1} car^{-1} were obtained for zinc, copper, lead, nickel and vanadium. The emission factors of these trace metals showed very high variation and, excluding nickel, good correlation with each other, which could be explained with the utilization of these metals in brake linings and the fact that emission by brake lining wear depends strongly on the driving mode. An average emission factor of 7.1 ng km^{-1} car^{-1} was obtained for palladium, which is the first value for palladium obtained under real world conditions. This emission factor was more stable during the sampling period than the emission factor of the other trace metals and was in the range of values found in dynamometer studies.

Using the determined emission factors the emission ratio between individual aerosol constituents and palladium were calculated. These values could be used to estimate the contribution of traffic pollutants to the total concentration present at other sampling sites.

For the application of this tracer model additional sampling campaigns were conducted in Oberwart and Vienna. In Oberwart palladium concentrations were below detection limit. In Vienna compound concentrations were generally comparable to the tunnel outside site. Emission ratios between palladium and other components were calculated from emission factors obtained in the tunnel study. The application of the emission ratios between pollutants and palladium led to a high overestimation of pollutant concentrations, especially for particulate matter, total carbon, black carbon, organic carbon and copper.

An explanation for the failure of the tracer model could be given by the differences in the driving conditions at the investigated sampling sites. The emission of palladium containing particles by the car catalyst was found to depend on driving conditions and the age of the catalyst in dynamometer studies, which would explain the failure of the application of the emission ratios found in the tunnel to samples collected in the inner city of Vienna, since the dominating driving mode in the tunnel is free cruising at 80 kilometres per hour, in contrast to the stop-and-go conditions that dominate the driving in the inner city of Vienna.

Conclusion:

Palladium can be principally used as tracer for traffic emissions, because it was shown that the palladium concentration is not influenced by other sources. Because of the dependency of the emission factor of palladium and other pollutants on the driving mode it is necessary to obtain emission factors under stop and go conditions which can then be applied on urban samples. Further the emission ratios found in the Kaisermühlen tunnel must be applied on samples collected near free ways with cruising conditions to finally proof the applicability of the palladium tracer model.

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Tunnel inside:

Gasmeter, traffic density and air velocity

Quartz fibre filter					Traffic and air velocity		
Date	Gasmeter l	T (°C)	m³	Nm³	LDV	HDV	v (m/s)
17.9.	2605613	23.5	11.7	10.8			
18.9.	2617351	23.5	12.5	11.5	43973	8575	5.79
19.9.	2629827	21.1	12.6	11.7	44281	8316	5.85
20.9.	2642397	21.4	12.7	11.8	38518	6011	5.50
21.9.	2655121	20.6	12.4	11.3	36086	3079	6.35
22.9.	2667475	30.3	12.7	11.4	38520	4446	5.53
23.9.	2680146	30.2	12.1	11.1	43134	8156	6.77
24.9.	2692217	17.5	11.9	11.2	43915	8123	6.44
25.9.	2704093	15.7	11.8	11.2	44617	7976	6.60
26.9.	2715890	14.8	11.0	10.4	45021	8005	6.68
27.9.	2726861	16.3	11.4	10.8	41712	5936	5.67
28.9.	2738279	15.7	10.9	10.4	35715	2460	4.70
29.9.	2749225	15.6	10.8	10.2	43089	4021	5.48
30.9.	2759997	15.4	10.8	10.2	44839	7893	6.42
1.10.	2770769	15.9	10.5	9.9	44593	7431	6.43
2.10.	2781265	16.2	10.4	9.8	44956	8086	6.43
3.10.	2791620	16.4	10.7	10.1	44475	8033	6.32
4.10.	2802353	18.3	10.5	9.8	41147	5750	5.50
5.10.	2812832	17.2	10.3	9.7	35250	2469	4.83
6.10.	2823096	17.0	10.2	9.6	39166	3685	5.45
7.10.	2833297	15.2	9.8	9.3			
8.10.	2843130	14.1					

Cellulose ester filter 1				
Date	Gasmeter l	T	m³	Nm³
17.9.	5143305	26.5	44.5	40.6
18.9.	5187794	26.5	46.4	42.3
19.9.	5234222	26.3	45.8	41.7
20.9.	5280040	27.2	47.4	43.1
21.9.	5327413	26.4	46.9	42.8
22.9.	5374317	25.3	49.4	45.3
23.9.	5423684	24.4	45.4	42.0
24.9.	5469090	20.0	45.6	42.4
25.9.	5514682	20.6	46.7	43.5
26.9.	5561370	20.0	46.1	42.9
27.9.	5607506	21.3	47.4	44.0
28.9.	5654879	20.9	46.9	43.6
29.9.	5701766	20.5	47.0	43.7
30.9.	5748770	20.2	46.8	43.5
1.10.	5795520	20.6	45.7	42.5
2.10.	5841262	21.1	46.2	42.9
3.10.	5887470	21.1	45.5	42.1
4.10.	5932994	22.8	46.4	42.9
5.10.	5979375	22.0	47.0	43.5
6.10.	6026397	21.9	48.3	44.9
7.10.	6074741	20.0	46.1	43.1
8.10.	6120883	18.5		

Cellulose ester filer 2						
Date	Gasmeter [l]	m³	T (°C)	Δp start (bar)	Δp end (bar)	Nm³
17.9.	1088928	138.7	23.2	0.38	0.44	76.5
18.9.	1227626	149.1	20.2	0.40	0.57	72.3
19.9.	1376709	146.2	20.5	0.38	0.55	73.7
20.9.	1522891	147.8	19.2	0.40	0.57	72.1
21.9.	1670729	148.2	18.5	0.40	0.56	73.0
22.9.	1818945	156.1	18.7	0.40	0.55	77.8
23.9.	1975000	145.2	17.1	0.39	0.54	74.1
24.9.	2120214	145.9	15.5	0.39	0.54	75.0
25.9.	2266081	149.4	13.3	0.38	0.54	77.4
26.9.	2415464	147.5	16.0	0.38	0.54	76.3
27.9.	2562925	150.9	14.1	0.38	0.54	78.6
28.9.	2713859	149.8	14.7	0.38	0.54	77.7
29.9.	2863688	151.0	13.9	0.40	0.58	74.4
30.9.	3014730	149.2	15.4	0.41	0.58	72.2
1.10.	3163930	148.3	15.7	0.40	0.59	71.6
2.10.	3312201	144.5	16.1	0.40	0.58	70.3
3.10.	3456679	145.4	17.0	0.40	0.58	70.8
4.10.	3602094	146.0	16.3	0.40	0.58	71.2
5.10.	3748068	148.5	15.8	0.40	0.58	72.7
6.10.	3896613	154.6	14.5	0.40	0.54	78.9
7.10.	4051176	146.4	12.5	0.40	0.56	75.3
8.10.	4197585					

Solution concentrations and filter aliquots:

	Cellulose 1		quartz fibre filter aliquot (9/40)^2			Cellulose 1	Cellulose 2
	filter weight before sampling	after sampling	TC	BC	OC	Pd	Pd
Date	Mg		µg			ppt	
18.9.	67.57	72.82	46.0	29.9	16.1	155	
19.9.	67.80	73.88	50.7	32.5	18.2	182	
20.9.	67.00	72.96	46.0	30.8	15.2		295
21.9.	68.09	72.96	39.5	25.5	14.0	176	293
22.9.	66.35	71.27	38.9	26.4	12.6	108	
23.9.	66.42	72.18	43.1	30.2	12.9	128	
24.9.	66.84	72.15	42.1	27.7	14.4	103	
25.9.	66.75	72.08	43.2	29.6	13.6	90	
26.9.	66.74	72.41	38.7	26.1	12.7	178	
27.9.	66.77	71.23	36.3	24.2	12.1	128	
28.9.	67.12	70.82	31.3	19.5	11.8	218	267
29.9.	67.23	71.59	35.6	21.5	14.1	182	220
30.9.	67.09	72.52	41.4	26.0	15.5	150	
1.10.	66.83	73.68	41.9	28.0	13.9	196	
2.10.	66.72	73.78	44.4	29.5	14.8	222	
3.10.	67.54	74.44	46.4	30.5	15.9	82	250
4.10.	67.16	72.26	35.7	22.1	13.6	213	
5.10.	67.34	71.05	25.4	17.7	7.7	204	144
6.10.	67.02	72.08	49.0	29.7	19.3	299	212
7.10.	67.21	72.21	36.5	23.9	12.5	233	

	Zn	Cu *	Pb *	Cd	Ni	V	quartz fibre filter aliquot
	ppb						
18.9.	80	13.4	5.4	0.02	2.4	2.3	0.49
19.9.	90	20.6	5.9	0.16	6.4	2.5	0.42
20.9.	100	13.1	5.5	0.05	3.0	4.3	0.46
21.9.	120	16.2	6.7	0.06	7.8	4.3	0.43
22.9.	70	8.0	3.8	0.05	3.1	1.5	0.40
23.9.	80	9.7	6.5	0.11	1.2	2.6	0.46
24.9.	80	10.5	6.2	0.11	9.2	2.7	0.44
25.9.	80	10.8	4.9	0.12	3.7	2.1	0.45
26.9.	110	12.6	4.1	-0.01	4.6	4.4	0.44
27.9.	45	6.7	2.6	0.02	1.3	1.6	0.44
28.9.	50	6.7	3.4	0.04	2.8	2.4	0.43
29.9.	100	13.9	5.8	0.05	5.3	3.6	0.42
30.9.	85	18.3	7.7	0.12	10.8	4.5	0.44
1.10.	90	17.9	7.2	0.14	3.9	5.2	0.45
2.10.	220	35.2	15.7	0.25	9.8	7.4	0.44
3.10.	160	22.7	10.0	0.08	6.8	6.5	0.40
4.10.	110	14.3	5.4	0.02	2.9	3.4	0.43
5.10.	65	11.8	4.6	0.02	2.4	2.0	0.43
6.10.	100	12.4	4.7	0.02	2.3	4.4	0.43
7.10.	75	12.0	4.0	0.00	3.6	2.2	0.41

*Due to high concentrations of copper and lead the stock solution was diluted 1:4 before the measurement

Concentrations in air:

	PM	TC	BC	OC	Pd
	µg/m³				Pg/m³
18.09.02	186.4	78.7	51.2	27.5	18.3
19.09.02	124.0	85.8	55.1	30.8	21.8
20.09.02	145.7	76.8	51.5	25.4	20.4
21.09.02	138.2	69.0	44.5	24.5	20.0
22.09.02	113.7	67.4	45.7	21.8	11.9
23.09.02	108.7	76.7	53.8	22.9	15.2
24.09.02	137.2	74.3	48.9	25.4	12.1
25.09.02	125.1	76.4	52.3	24.1	10.3
26.09.02	122.6	73.7	49.6	24.1	20.8
27.09.02	132.2	66.5	44.4	22.1	17.2
28.09.02	101.4	59.7	37.1	22.5	14.8
29.09.02	84.9	69.0	41.6	27.4	20.8
30.09.02	99.7	80.4	50.4	30.0	17.3
01.10.02	124.8	83.5	55.7	27.8	23.0
02.10.02	161.2	89.7	59.7	29.9	11.8
03.10.02	164.6	90.8	59.7	31.1	17.6
04.10.02	163.7	71.7	44.5	27.3	10.8
05.10.02	119.0	51.9	36.2	15.7	9.9
06.10.02	85.2	100.5	60.8	39.6	13.4
07.10.02	112.7	77.2	50.6	26.5	11.8

	Zn	Cu	Pb	Ni	V
	ng/m^3				
18.09.02	63.5	44.1	21.8	0.0	0.3
19.09.02	84.9	83.7	27.4	3.9	0.6
20.09.02	86.8	44.5	23.2	0.0	2.4
21.09.02	120.9	64.8	31.4	5.6	2.6
22.09.02	65.9	27.6	18.7	0.0	0.0
23.09.02	70.0	32.6	28.8	0.0	0.7
24.09.02	72.6	37.2	28.6	7.0	0.8
25.09.02	71.6	38.1	22.3	0.7	0.1
26.09.02	116.4	50.8	20.6	1.9	3.0
27.09.02	34.6	20.9	12.8	0.0	0.0
28.09.02	42.4	22.1	17.5	0.0	0.6
29.09.02	110.5	60.8	31.0	3.0	2.1
30.09.02	85.3	79.0	38.2	9.5	3.2
01.10.02	92.9	78.4	36.4	1.1	4.1
02.10.02	267.5	172.6	82.7	8.9	7.0
03.10.02	200.1	113.6	56.1	5.3	6.3
04.10.02	124.9	63.9	28.9	0.0	1.9
05.10.02	66.8	51.5	25.6	0.0	0.0
06.10.02	112.9	54.5	25.5	0.0	3.2
07.10.02	87.1	57.2	23.8	0.8	0.3

Tunnel outside:

Gasmeter:

Quartz fibre filter					
Date	Gasmeter [l]	m³	T	Nm³	T/
18.9.	4452543	27.8	17.3	26.2	16.95
20.9.	4480371	28.5	16.6	27.0	15
22.9.	4508878	28.9	13.4	27.4	14.75
24.9.	4537729	28.7	16.1	27.3	14.2
26.9.	4566422	28.7	12.3	27.4	13.05
28.9.	4595141	28.8	13.8	27.5	13.6
30.9.	4623958	29.0	13.4	27.6	14
2.10.	4652923	28.3	14.6	26.7	16.55
4.10	4681221	28.7	18.5	27.0	16.75
6.10.	4709891	29.0	15	27.6	14.05
8.10.	4738875		13.1		

Cellulose ester filter 1				
Date	Gasmeter [l]	m³	T (°C)	Nm³
18.9.	2478971	101.1	22.3	93.8
20.9.	2580050	101.1	20.0	94.5
22.9.	2681198	101.5	18.5	95.1
24.9.	2782697	100.8	18.2	95.0
26.9.	2883493	101.8	15.3	96.1
28.9.	2985274	102.2	16.8	96.4
30.9.	3087497	102.3	16.0	96.4
2.10.	3189802	97.3	17.2	91.0
4.10	3287145	102.0	21.2	95.2
6.10.	3389167	51.9	17.9	49.0
8.10.	3441060		14.6	

Cellulose ester filter 2						
Date	Gasmeter [l]	m^3	T (°C)	Δp start (bar)	Δp end (bar)	Nm^3
18.9.	36500825	347.0	17.5	0.44	0.54	169.2
20.9.	36847833	353.3	14.8	0.43	0.52	177.9
22.9.	37201097	358.1	13.3	0.43	0.47	190.1
24.9.	37559230	350.2	12.5	0.44	0.45	188.0
26.9.	37909435	350.1	10.2	0.44	0.48	183.6
28.9.	38259563	353.9	12.4	0.45	0.47	185.3
30.9.	38613436	346.9	10.9	0.44	0.52	174.7
2.10.	38960293	334.7	13.6	0.44	0.57	158.8
4.10	39294993	346.2	15.8	0.44	0.54	169.5
6.10.	39641240	352.8	14.1	0.44	0.48	184.6
8.10.	39993995		9.5			

Solution concetrations and filter aliquots

	cellulose ester filter 1	quartz fibre filter aliquot $(9/40)^2$				Cellulose 1	Cellulose 2
Date	filter weight before sampling	after sampling	TC	BC	OC	Pd	Pd
	Mg	µg				ppt	
18.9.	68.03	74.35	19.6	9.2	10.3	162	-
20.9.	68.00	71.93	12.4	4.9	7.5	70	-
22.9.	67.16	72.50	13.5	6.4	7.1	59	-
24.9.	66.70	72.11	14.1	6.2	7.9	32	104
26.9.	66.73	69.15	9.6	4.5	5.1	130	84
28.9.	66.89	69.70	13.8	6.6	7.3	167	215
30.9.	66.62	74.55	28.1	15.0	13.1	167	-
2.10.	66.07	74.49	32.2	14.0	18.2	165	-
4.10	67.12	71.01	11.4	3.9	7.5	-	230
6.10.	67.29	68.84	11.2	4.9	6.3	113	65

Date	Zn	Cu*	Pb*	Cd	Ni	V	quartz fibre filter-aliquot
	ppb						
18.9.	95	15.1	7.8	0.32	7.4	9.5	0.49
20.9.	55	4.3	4.2	0.10	3.0	4.3	0.51
22.9.	175	9.4	11.7	0.35	17.9	6.0	0.52
24.9.	65	3.5	6.3	0.27	1.7	2.1	0.50
26.9.	100	7.6	4.6	0.24	5.9	2.3	0.54
28.9.	100	9.8	7.5	3.64	13.2	2.8	0.50
30.9.	240	15.8	18.7	0.52	4.3	8.7	0.51
2.10.	265	14.5	21.4	0.42	10.0	11.8	0.52
4.10	80	6.1	4.8	0.10	2.2	3.4	0.50
6.10.	90	7.7	4.2	0.09	4.0	2.5	0.51

*Due to high concentrations of copper and lead the stock solution was diluted 1:4 before the measurement

Concentrations in air :

Date	Particle mass	TC	BC	OC	Pd
	µg/m³				pg\m³
18.09.02	67.4	14.7	7.0	7.8	8.6
20.09.02	41.6	9.0	3.6	5.4	3.7
22.09.02	56.1	9.7	4.6	5.1	3.1
24.09.02	57.0	10.2	4.5	5.7	2.8
26.09.02	25.2	6.9	3.2	3.7	2.3
28.09.02	29.1	9.9	4.7	5.2	5.8
30.09.02	82.2	20.2	10.7	9.4	8.2
02.10.02	92.6	23.8	10.3	13.5	4.5
04.10.02	40.9	8.3	2.9	5.4	6.8
06.10.02	31.6	8.0	3.5	4.5	1.8

Date	Zn	Cu	Pb	Ni	V
	ng/m³				
18.09.02	34.3	22.2	13.6	1.9	3.3
20.09.02	15.9	3.3	6.9	0.0	0.9
22.09.02	63.2	11.3	18.8	5.9	1.6
24.09.02	20.1	1.9	10.5	0.0	0.0
26.09.02	32.1	8.1	7.2	1.1	0.1
28.09.02	34.2	12.2	12.4	4.1	0.3
30.09.02	89.3	21.5	29.9	0.5	2.7
02.10.02	99.9	19.6	34.4	2.8	3.9
04.10.02	26.5	6.2	8.0	0.0	0.6
06.10.02	29.3	8.5	6.8	0.4	0.2

Oberwart:

Gasmeter:

Cellulose ester filter				
Date	Gasmeter (l)	T (°C)	m^3	Nm^3
3.11.	1716257	21.5	61.28	57.62
4.11.	1777540	13.2	59.71	57.19
5.11.	1837245	10.8	59.43	57.09
6.11.	1896674	11.6	59.25	56.85
7.11.	1955919	11.4	59.87	57.72
8.11.	2015786	8.9	58.88	56.60
9.11.	2074665	13.1	57.17	54.55
10.11.	2131832			

Quartz fibre filter				
Date	Gasmeter l	T (°C)	m^3	Nm^3
3.11.	3236185	21.9	54.70	51.63
4.11.	3290880	10.5	54.66	52.92
5.11.	3345536	7.4	53.64	52.10
6.11.	3399176	8.7	53.55	51.83
7.11.	3452728	9.5	53.57	51.90
8.11.	3506302	8.1	53.77	51.98
9.11.	3560067	10.7	51.80	49.84
10.11.	3611862			

Solution concentrations and filter aliquots

	cellulose filter		quartz fibre filter aliquot $(9/40)^2$			Cellulose filter
Date	filter weight before sampling	after sampling	TC	BC	OC	Pd
	Mg		µg			ppt
3.11.	66.71	67.92	14.8	6.5	8.3	b.d.
4.11.	66.90	67.98	15.0	6.8	8.2	b.d.
5.11.	66.89	67.93	15.7	6.4	9.3	b.d.
6.11.	66.35	68.33	30.8	12.6	18.2	b.d.
7.11.	66.63	68.70	37.4	14.7	22.7	b.d.
8.11.	66.84	69.53	46.4	18.0	28.4	b.d.
9.11.	66.89	68.43	25.7	9.8	15.9	b.d.

Date	Zn	Cu*	Pb*	Cd	Ni	V	quartz fibre filter aliquot
	Ppb						
3.11.	120	5.9	12.8	1.00	15.3	3.2	0.50
4.11.	40	12.8	5.4	0.44	4.2	0.6	0.51
5.11.	90	4.2	10.9	0.38	7.9	4.3	0.51
6.11.	155	6.4	17.0	0.57	8.9	5.0	0.51
7.11.	150	6.0	12.1	0.40	6.1	3.7	0.50
8.11.	280	8.4	15.6	0.50	15.3	7.6	0.50
9.11.	60	4.2	5.1	0.33	4.2	2.5	0.48

*Due to high concentrations of copper and lead the stock solution was diluted 1:4 before the measurement

Concentrations in air

Date	Pm	TC	BC	OC	Pd
	μg/m³				pg/m³
3.11	21.0	5.7	2.5	3.2	b.d.
4.11	18.9	5.6	2.6	3.1	b.d.
5.11	18.2	6.0	2.4	3.5	b.d.
6.11	34.8	11.8	4.8	6.9	b.d.
7.11	35.9	14.2	5.6	8.7	b.d.
8.11	47.5	17.6	6.8	10.8	b.d.
9.11	28.2	10.2	3.9	6.3	b.d.

Date	Zn	Cu	Pb	Cd	Ni	V
	ng/m³					
3.11	22.8	3.1	11.3	0.55	2.7	0.28
4.11	5.0	8.7	4.6	0.07	0.2	< blank
5.11	15.7	1.6	9.3	0.02	1.0	0.50
6.11	29.4	3.5	14.4	0.18	1.2	0.64
7.11	28.8	3.2	10.5	0.03	0.7	0.37
8.11	57.1	5.3	13.5	0.11	2.7	1.22
9.11	10.2	1.7	4.8	< blank	0.3	0.12

TU Vienna:

Gasmeter:

Cellulose ester filter				
Date	Gasmeter [l]	T (°C)	m^3	Nm^3
23.10.	2862178	23.7	63.16	58.03
24.10.	2925334	24.6	61.37	55.86
25.10.	2986699	29.2	63.33	57.98
28.10.	3050030	21.2	60.81	56.73
29.10.	3110836	18.1	61.80	57.72
30.10.	3172637	20.5	63.53	59.09
31.10.	3236165			

Quartz fibre filter				
Date	Gasmeter l	T	m^3	Nm^3
23.10.	1387957	22.7	55.17	50.85
24.10.	1443131	23.8	54.53	49.65
25.10.	1497665	29.9	55.84	51.00
28.10.	1553501	21.9	52.95	49.56
29.10.	1606451	15.5	53.55	50.17
30.10.	1659997	21.3	56.24	52.17
31.10.	1716232			

Solution concentrations and filter aliquots:

	cellulose filter		quartz fibre filter aliquot $(9/40)^2$			Cellulose filter
Date	filter weight before sampling	after sampling	TC	BC	OC	Pd
	mg		µg			ppt
23.10.	67.14	69.94	43.6	22.9	20.8	160
24.10.	66.79	69.92	50.9	26.8	24.1	103
25.10.	67.03	69.03	32.8	14.7	18.1	11
28.10.	66.82	69.76	35.1	19.1	16.0	156
29.10.	67.15	70.61	44.9	19.7	25.3	60
30.10.	66.88	69.80	43.3	21.5	21.8	63

Date	Zn	Cu*	Pb*	Cd	Ni	V	Quartz fibre filter aliquot
	ppb						
23.10.	120	19.2	15.7	0.07	6.6	5.2	0.49
24.10.	290	37.5	21.4	0.15	33.9	12.6	0.53
25.10.	80	15.1	8.2	0.29	13.3	6.4	0.48
28.10.	530	44.9	34.8	0.27	36.4	15.5	0.51
29.10.	265	30.2	25.1	0.49	22.9	13.2	0.52
30.10.	165	8.6	3.0	0.22	14.9	2.3	0.52

*Due to high concentrations of copper and lead the stock solution was diluted 1:4 before the measurement

Concentrations in air

Date	PM	TC	BC	OC	Pd
	µg/m^3				Pg/m^3
23.10	48.3	16.9	8.9	8.1	13.9
24.10	56.0	20.2	10.6	9.6	9.4
25.10	34.5	12.7	5.7	7.0	1.3
28.10	51.8	14.0	7.6	6.4	13.7
29.10	59.9	17.7	7.7	9.9	5.2
30.10	49.4	16.4	8.1	8.2	5.3

Date	Zn	Cu	Pb	Ni	V
	ng/m^3				
23.10	23.4	15.2	14.2	0.8	0.7
24.10	58.1	29.8	18.2	6.5	2.3
25.10	14.5	11.6	7.6	2.3	1.0
28.10	113.2	37.5	30.7	7.3	3.0
29.10	53.8	24.2	21.8	4.3	2.4
30.10	30.7	5.1	2.6	2.5	0.1

Field blancs

Zn	Cu	Pb	Cd	Ni	V	filter aliquot
ppb						
30	3.6	0.5	1.58	3.1	1.6	0.50
0	0.7	-0.1	0.00	-0.9	1.2	0.50
20	0.5	-0.3	0.15	8.4	1.0	0.53
20	5.9	-0.1	0.05	3.2	3.1	0.42
10	0.7	-0.3	0.03	1.4	3.1	0.40
Average						
16	2.3	-0.1	0.36	3.0	2.0	0.47

Palladium and the carbonaceous fraction field blanc values were negligible.