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Transverse approach between real world concentrations of SO₂, NO₂, BTEX, aldehyde emissions and corrosion in the Grand Mare tunnel

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Abstract

With regard to automotive traffic, a tunnel-type semi enclosed atmosphere is characterized by a higher concentration of gaseous pollutants than on urban traffic roads and highlights the gaseous effluent species having an impact on material degradation. Therefore, a transverse approach between air quality and its consequences upon the longevity of materials is necessary, implying better knowledge of tunnel atmosphere and a better understanding of material degradation inside a tunnel for operating administration. Gaseous pollutant measurements carried out in a road tunnel in Rouen (Normandy) give the real world traffic concentrations of experimental exposure conditions. The sampling campaigns, achieved in summer and winter include SO₂, NO₂, BTEX and aldehyde analyses. Effluent profiles in the upward and downward tubes have been established. The current work shows that SO₂, NO₂, formaldehyde, acetaldehyde, propanal and butanal must be considered in the degradation process of materials in a stuffy environment. As regards NO₂, its concentration depends on the modification of the automotive fleet. The total aldehyde concentrations indicate no particular trend between the two bores. Formaldehyde, acetaldehyde, propanal, butanal and acrolein species are the most abundant species emitted by vehicles and represent 90% to 95% of the total aldehyde emissions.

Key words: SO₂; tunnel study; aldehydes; NO₂; BTEX; atmospheric corrosion

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Introduction

Road traffic is one of the largest sources of air pollutants in the urban environment. The organic and inorganic gaseous effluents such as NOx, volatile organic compounds (VOCs) and aldehydes are the precursors of health troubles in ambient conditions. Intensive research is consequently focused on particles and gaseous pollutant emissions. There are two methods to determine vehicular emission profiles: the first consists in carrying out dynamometric tests on individual vehicles and the second consists of outdoor studies near heavy traffic roads or in a road tunnel. The tunnel studies give us a determination of the average emission of a large number of vehicles. The emission factor used to describe the automotive emission is determined by the amount of emitted air pollutants per distance covered or per volume of fuel consumed.

So far, literature shows some tunnel studies conducted in several countries such as The United States: Van Nuys Tunnel (Fraser et al., 1998), Tuscarora tunnel (Pierson et al., 1996; Sagebriel et al., 1996; Grosjean et al., 2001), Fort Mc Henry tunnel (Pierson et al., 1996), Cassiar tunnel (Gertler et al., 1997), Asian countries: Shin Min

tunnel (Cheng et al., 2006; Ho et al., 2007), Tapei tunnel (Hwa et al., 2002) and European countries: Gubrist tunnel (Staehelin et al., 1995, 1998; Colberg et al., 2005), Tauern-tunnel (Schimd et al., 2001), Söderledstunnel (Johansson et al., 1997; Kristensson et al., 2004). Few studies were conducted in France (Touaty et al., 2000). As the composition of the vehicle fleet, motor improvements, catalytic technologies and the types of fuel change and potentially cause variations in the emissions, all the measurements have to be repeated.

Nevertheless, in the opposition to studies of air pollutant impacts on human health and the environment, no study has shown the relationship between air quality and the degradation of metallic materials exposed to stuffy environments.

Some studies concentrating upon the corrosion of materials such as copper, zinc or nickel have been achieved during outside exposure or laboratory studies with controlled gas concentration tests. From outside field exposition campaigns, one of the major results obtained is that the knowledge of both adhering layers and dissolved corrosion products during rainy periods is necessary to understand the degradation mechanism of the substrate. The analysis of corrosion products grown on copper or zinc coupons exposed in town centre areas indicates the

formation of hydroxy sulphate salts (Jouen, 2000; Jouen et al., 2000; Lefez et al., 2001). SO_2 levels have been progressively reduced in the automotive emissions and even though comparatively lower than industrial sources, they are still involved in material degradation. Laboratory studies have investigated the effects of SO_2, NO_2, O_3, in a mixed atmosphere as ($NO_2 + SO_2$) or ($SO_2 + O_3$) on various substrates such as copper, zinc or nickel. First of all, nitrogen oxides have an influential impact on human health. This gaseous species is a powerful oxidizing agent, very irritating for alveolus and branched membranes. It also has an effect on cardiovascular apparatus and particularly on blood coagulation. According to the World Health Organisation, a one-hour exposure to NO_2 concentrations beyond 200 $\mu g/m^3$ leads to a risk for human health. Otherwise, nitrogen dioxide is also an influent factor in the degradation process of materials (Svendung et al., 1983; Svensonn et al., 1993; Zakipour et al., 1995; Zakipour et al., 1997; Castaño et al., 2007; Mariaca et al., 2008). The corrosive effect of NO_2 acting alone depends greatly on the relative humidity (RH) (Mariaca et al., 2008). At lower humidities, NO_2 is aggressive on copper substrates causing localised attacks. As regards zinc substrate, the corrosive action of NO_2 alone is negligible compared to SO_2 impact. The nitrogen dioxide does not contribute systematically to the formation of hydrated nitrate salts. An accelerating effect has been observed on copper and zinc substrates when NO_2 acts in conjunction with SO_2 (Svensonn et al., 1993; Oesch et al., 1997; Castaño et al., 2007). Therefore, we have included this parameter in our study. The influence of O_3 in combination with SO_2 is also important on the atmospheric degradation of some materials such as copper or zinc (Zakipour et al., 1995; Strandberg et al., 1997). As for hydrated organic salts, report in corrosion products is rare. Muller et al. (1997) have identified considerable amounts of organic compounds in soluble components of copper patina coming from the Statue of Liberty. The most abundant organic products were carboxylates and mainly acetate. The effect of aldehyde and organic acids on the atmospheric corrosion of metals has been explored. Carboxylate salts are the main corrosion products developed in laboratory exposure with high concentrations of formaldehyde and acetaldehyde as well as formic and acetic acids (Knotkova et al., 1990).

This work is part of a project dealing with the degradation of materials in a semi enclosed tunnel-type atmosphere and with the equipment reliability and lifetime. The understanding of corrosion mechanisms involves knowledge of the real conditions of materials exposure, identification and quantification of gaseous pollutants. The presence of potent oxidizing species absorbed in an aqueous film formed during wet periods on the substrate surface contributes to the achievement of the degradation process based on successive steps of dissolution and then re-precipitation. The characterization of the real atmospheric exposition conditions must be made during a long and adequate period. We followed the composition of the atmosphere from the Grand Mare tunnel (France), SO_2-NO_2-BTE-aldehydes, taking into account possible

differences induced by the season or the slope of traffic lanes. No distinction of vehicle type or engine has been made owing to the fact that the counting during a long period is more tedious. The emission factors were calculated strictly for the comparison with the experimental results published in literature.

1 Methodology

1.1 Grand Mare tunnel

The Grand Mare tunnel is an urban tunnel parted in two separate tubes (north bore and south bore) with two traffic lanes per bore and currently used by around 41,500 vehicles per day (2008 traffic count). Vehicles are only distinguished by their length: 12% of heavy-duty vehicle (> 5 m) and 88% of low duty vehicles. The tunnel length is around 1532 m with a slope of ca. 3% (Fig. 1). Each tube has a cross section of 51 m^2. The vehicle speed limit is 70 km/hr. Both tubes are equipped with a ventilation system which is not in operation during the entire sampling period. The ventilation mode is longitudinal and caused by the piston effect of the traffic flow. Referring to the data resulting from the acquisition of measurements of wind speed during the two campaigns, a little variation between the values was observed so that we have considered in the following calculation the mean value of 5.7 m/sec (standard deviation 1.2 m/sec) as air velocity in the downward tube and 5.4 m/sec (standard deviation of 0.9 m/sec) as air velocity in the upward tube.

1.2 Sampling

Two sampling campaigns (atmosphere control, metallic coupons exposition) were conducted: the first took place in summer (from May 3 to July 16, 2007) and the second took place in winter (from January 23 to April 24, 2009). Only the results concerning the analysis of gaseous effluents are presented in this article. Three locations were chosen for both campaigns UA, UC, DA as shown in Fig. 1. Thermo hygrometric conditions were simultane-
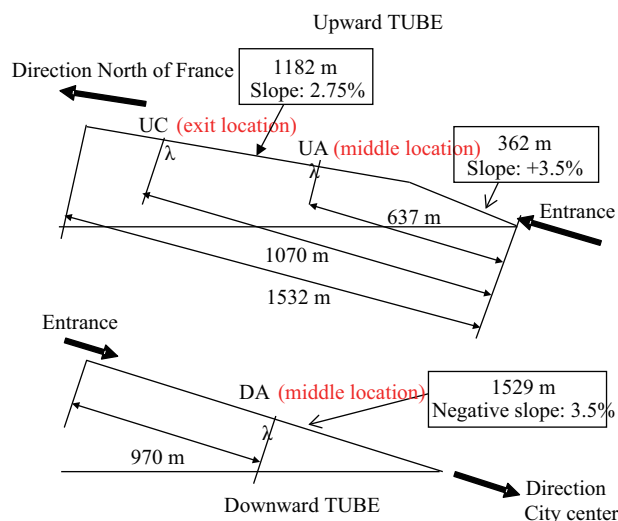

Fig. 1 Geometrical characteristics of Grand Mare urban tunnel and sampling locations in upward and downward tubes.

ously registered using a Vaisala transductor HUMICAP HMT 330. The average values of relative humidity and temperature recorded during the two sampling campaigns are respectively 65% and 17°C (range: 44%–90%, 14–25°C) in summer, 71% and 9°C (range: 40%–97% , 0–16°C) in winter.

Sampling of air pollutants were carried out by means of passive samplers, exposed on a weekly basis that gives cumulative values. The samplers, Radiello® diffusive tubes were installed on the specific exposition stands fixed on the tunnel wall at a height of 1.5 m and at a length of 0.5 m from the traffic left line.

The Radiello® sampler consisted of a compound-specific adsorbing cartridge (a rod), surrounded by a cylindrical micro porous diffusive body. The characteristics of the adsorbing cartridge and diffusive body are depending on the polluting species to be sampled.

1.3 Chemical analyses

For NO_2 and SO_2, the cartridge consisted of a 5.8 mm-diameter and 60 mm-long micro porous polyethylene tube coated with triethanolamine (TEA). Nitrogen (NO_2) and sulphur (SO_2) dioxide were chemiadsorbed onto TEA: nitrite (NO_2^-) and sulphite (SO_3^{2-}) or sulphate (SO_4^{2-}) ions respectively.

Nitrite, sulphite and sulphate were recovered from the cartridges by means of extraction in 5 mL of ultrapure water (15 MΩ) followed by a 1-min manual stirring step.

The nitrite content of the extract was finally quantified by visible spectrophotometry. The sulphite and sulphate content of the extract was determined by ion chromatography.

For aldehydes, the adsorbing layer of the cartridge consisted of a stainless steel net cartridge filled with 2,4-dinitrophenylhydrazine (2,4-DNPH) coated Florisil®. Aldehydes react with 2,4-DNPH to give the corresponding 2.4-dinitrophenylhydrazones. The 2,4-DNPH was quantitatively recovered from the cartridge by means of extraction in 2 mL acetonitrile followed by a 30-min occasional stir. The resulting solution was filtered (0.45 μm), then analysed by reverse phase High-performance liquid chromatography (HPLC) and UV detection. No pretreatment before aldehyde analysis such as the elimination of ozone or particulate matter has been made. In the tunnel, the ozone concentration remains very low, below the detection limit. About dust, the porosity of diffusive body (25 μm) avoids any contamination with coarse particulate matter. Calibration curves for aldehydes were obtained with standard solutions (calibration solution from Sulpeco).

For BTEX, the adsorbing cartridge consisted of a 5.8-mm-diameter stainless steel net cylinder with a 100 mesh grid opening packed with (530 ± 30) mg of activated charcoal; particle size was 35 to 50 meshes. Volatile organic compounds were trapped by adsorption and recovered by carbon disulfide displacement. The analysis realized by Flame Ionization Detector (FID) gas chromatography was made by Fondazione Salvatore Maugeri laboratory. All the reagents used were of analytical grade.

All the measurements with ion chromatography were carried out on a Dionex model DX-100 ion chromatograph. The ions were detected by suppressed conductivity of the eluent using an ASRS-ULTRA self-regenerating suppressor.

For the separation of sulphur dioxide, an Ion Pac guard column, also produced by Dionex, was used. Data acquisition construction of calibration curves and peak integration were achieved with the Chromo Leon®Dionex software package.

Aldehyde sample analyses were performed on a Kontron HPLC chromatographic chain using a UV detector operated at a wavelength of 365 nm. Hydrazones separation was carried out on a Kromasil C18 column. The mobile phase was made of methanol and water at a flow rate of 1 mL/min.

1.4 Emission factor

The emission factor from tunnel measurements was calculated according to the method by Pierson et al. (1996). The vehicular emission factor can be determined from Eq. (1):

$$EF_{veh} = \frac{(C_i - C_0)S\,vt}{NL} \tag{1}$$

where, EF_{veh} (mg/(km·veh)) is the vehicular emission factor. C_i (mg/m^3) represents the concentration of specific air pollutant at sampling place and C_0 (mg/m^3) the background concentration at the tunnel entrance. S (m^2) is the area of the tunnel cross section. v (m/sec) is the wind speed and t (sec) is the sampling duration. N is the total traffic number during the sample period (overall fleet). L (km) is the distance between two sampling locations. In this study, the emission factor was only calculated between two sampling stations, namely the middle tunnel location (UA) and the exit tunnel position (UC) in the rising tube.

2 Results

2.1 Traffic count

Figure 2 shows the evolution of the average number of vehicles per hour crossing both tubes during the exposition campaigns of diffusive bodies (summer: May–Jul 2007, winter: Jan–Apr 2009). The density of vehicles includes different kinds of situations such as morning or afternoon traffic and rush-hour traffic peaks, constant traffic and low-density week end and night traffic. The traffic density is significantly higher in the upward tube than in the downward one, whatever the observation period (p_{summer} = 0.021; p_{winter} = 0.0005). In the same way, in the upward or downward ways, the traffic density average is not significantly different during the winter and summer periods (p_{upward} = 0.283; $p_{downward}$ = 0.078).

2.2 SO_2 evolution

The evolution of SO_2 concentration during summer 2007 and winter 2009 is illustrated in Fig. 3. For each sampling campaign, the average and standard deviation have been calculated to execute t-test with the standard confidence level of 95%. It shows that the average concentration
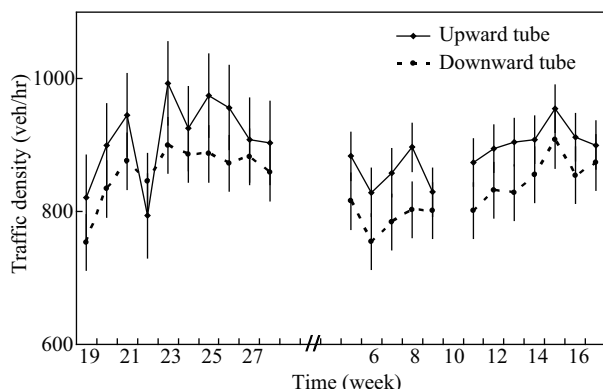
Fig. 2 Traffic density crossing the upward and downward tubes during the two sampling period. Week numbers 19–28 and 5–17 indicate periods of tests performed respectively in summer 2007 and winter 2009. Error bars represents standard deviation.

measured in the middle and at the exit of the tunnel in the upward direction is not significantly different, independently of the testing period (p_{summer} = 0.137, p_{winter}: 0.616). The values observed in the ascending tube are significantly higher than those determined in the descending tube during the two campaigns (p_{summer} = 0.0013; p_{winter} = 0.0014), and correlated with the slope of the Grand Mare tunnel. The engine power required to overcome the positive slope (ca. +3%) of the upward tube is higher than that required to pass through the downward tube (ca. –3.5%). The traffic density is significantly higher in the upward tube than in downward tube and the amount of gaseous effluent emitted is higher in upward tube compared to downward tube. Consequently, it explains the results obtained for SO₂. We do not observe "the pumping" effect on the SO₂ concentration. This pumping effect or piston effect is defined as the movement of air masses due to the movement of vehicles in the tunnel (no traffic: wind speed at ca. 0.8 m/sec; traffic wind speed at about 5.5 m/sec). The different statistical tests indicate that average concentrations measured in winter 2009 are significantly higher than those observed in summer 2007, in any case in the middle of the bores and at the exit. Higher values in winter can be associated with an increased use of air
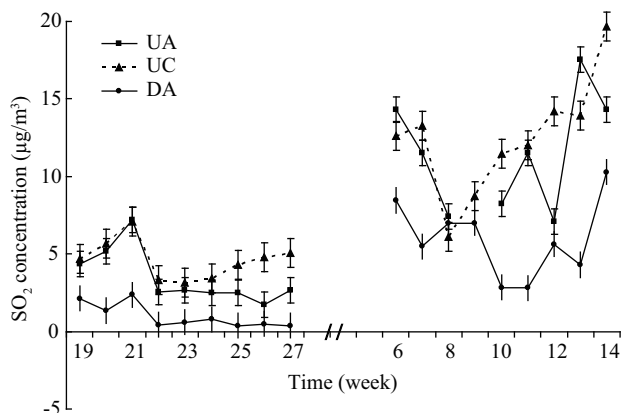
conditioning in the vehicles, the thermal regulation associated with engine operation and the increasing number of vehicles starting with a cold engine contributing to increase the fuel consumption. Table 1 shows the ratio of the average summer/winter concentrations, which remains constant throughout the tunnel. The values measured in the downward tube are lower than those in the upward tube, in summer and in winter, with a ratio summer/winter two times smaller.

Due to the limited published data, it is not really possible to compare our results with the emission factors of the literature, the only data being that of Staehelin et al. (1998) performed during one week in Sep 1993 (Table 2). Our results, determined for all vehicles, are in accordance to those calculated by Staehelin et al. (1998), taking into account the calculated uncertainties.

2.3 NO₂ concentration evolution

Figure 4 shows the evolution of NO₂ concentrations in summer 2007 and winter 2009. As previously, the average and standard deviation have been calculated for each sampling location in order to initiate *t*-test with a confidence level of 95%. For the two sampling campaigns, in the ascending tube, the average concentration (Table 1) at the exit of the bore is significantly higher than the value obtained in the middle of the bore (p_{summer}: 0.0245; p_{winter} = 0.038), thus highlighting the pumping effect. The average values in the ascending way are significantly higher than those determined in the descending way (p_{summer} = 0.0028; p_{winter} = 0.0002). The variability in the winter sampling campaign is high in the ascending tube while the traffic density and emitted particles account remain approximately unchanged. High relative humidity variation is suspected to affect temporarily the absorbent properties of the cartridge.

There is no detectable variation of the average concentration between summer and winter in the downward tube (ratio ca. 1) while an important difference is observed in the upward tube with a ratio around 0.8 (Table 1). The steady evolution of motor vehicles and the gradual renewal of the vehicle fleet since 2004 led to a gradual increase in the ratio NO₂/NO*x* although the NO*x* concentration remains approximately constant. This evolution is not

Fig. 3 SO₂ concentration evolution during summer 2007 and winter 2009 period. UA, UC and DA represent respectively the three sampling locations: middle position, exit position in upward tube and middle position in downward way. Summer 2007 campaign: week numbers 19–27 and winter 2009 sampling period: week numbers 5–14. Error bars: ± standard deviation.
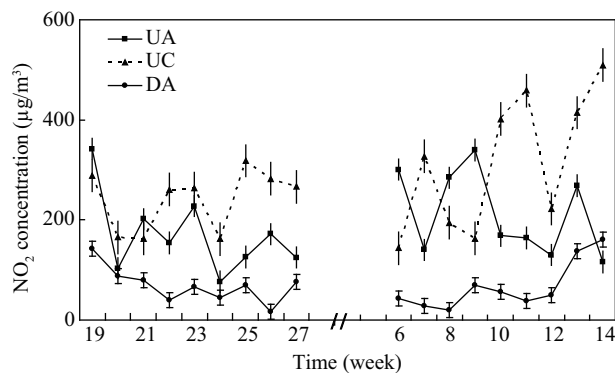

Fig. 4 NO₂ concentration evolution during summer 2007 and winter 2009 period. Summer 2007 campaign: week numbers 19–27 and winter 2009 sampling period: week numbers 5–14. Error bars: ± standard deviation.

Table 1   Average SO_2 and NO_2 concentration obtained during the two campaigns (unit: $\mu g/m^3$)

Location	Summer 2007		Winter 2009		Summer 2007/Winter 2009	
	SO_2	NO_2	SO_2	NO_2	SO_2	NO_2
UA	3.5 ± 1.7	169.6 ± 80.1	11.5 ± 3.8	212 ± 102	0.30	0.79
UC	4.6 ± 3.0	241.0 ± 60.9	12.4 ± 3.8	314.9 ± 134.2	0.37	0.75
DA	1 ± 0.8	69.3 ± 35.4	6 ± 2.5	67.2 ± 51.4	0.16	1.02

Table 2   Comparison of SO_2 and NO_2 emission factors (EFs) in different tunnel studies

	SO_2 (mg/(km·veh))	NO_2 (mg/(km·veh))	NOx (mg/(km·veh))	Reference
Grand Mare Tunnel Summer 2007	3.20 ± 2.1*	263 ± 115*		This study
Grand Mare Tunnel Winter 2009	11.6 ± 8.4*	589 ± 289*		This study
Shing Mun Tunnel 2004			878 ± 308	Ho et al., 2006
Tapei Tunnel 2002			900 ± 180	Hwa et al., 2002
Tauern Tunnel 2001			3131 ± 383	Schmid et al., 2001
Söderleds Tunnel Winter 98/99			1360 ± 30	Kristensson et al., 2004
Söderleds Tunnel Winter 95/96			1500 ± 100	Johansson et al., 1997
Cassiar Tunnel 97			1653	Gertler et al., 1997
Gubrist Tunnel 93	7.03 ± 18.89 (gasole vehicle)			Staehelin et al., 1998
Gubrist Tunnel 93			2248.3	Staehelin et al., 1995

* Represents the value of the 95% confidence intervals of each EF calculated in this study.

detectable in the downward tube with a negative slope contrary to the upward tube that requires engine power to cross the positive slope. The evolution of this ratio correlated with the increased amount of NO_2 according to time is in agreement with the modification of the automotive fleet.

A study of dynamic measurements of pollutant concentrations performed directly behind moving vehicles has been realized with embarked measurement systems during the same summer exposure period (May–Jul 2007), two rounds between 9:00 am and 4:00 pm (Morin et al., 2007). The nitrogen oxides data are summarized in Table 3. These data do not integrate the night and week-end traffic conditions. Thereby, it is not possible to correlate dynamic and stationary data indicated in Table 3 because sampling conditions are very distant. The concentrations obtained during short time exposure (around 2 min) are not characteristic of real conditions of material testing and cumulative effect according to time, they are characteristic of the emitted and maximal local limits able to be reached.

EFs of nitrogen dioxide for both tubes provided by literature are summarized in Table 2. Again our results can not be compared to the published ones because they concern nitrogen oxides NOx. No specific data exist about the NO_2 emission factor. However, according to the equivalence of NO_2/NOx and EF_{NO_2}/EF_{NOx} (emission factor) ratio,

from the nitrogen oxides data of Table 3 and EF_{NO_2} data of Table 2, we can deduce EF_{NOx}. The calculated value (EF_{NOx}: 1241 mg/(km·veh)) is comparable to those reported by Kristensson et al. (2004) (Table 2). We can notice from Table 2 that the NO_2 emission factor has doubled between 2007 and 2009, an increase that can be correlated with the progressive renewal of the automotive fleet.

2.4 Aldehyde concentration

Nine aldehydes (formaldehyde, acetaldehyde, acrolein, propanal, butanal, isopentanal, pentanal, hexanal and benzaldehyde) have been monitored in both tubes in winter. Figure 5 shows the evolution of the whole aldehyde concentrations according to time. No particular trend between both ways appears.

The average concentration of each aldehyde emission is summarized in Table 4 with the corresponding standard deviation. The average value of the whole aldehyde emission for the three sampling locations varies from 16.3 to 18.38 $\mu g/m^3$. The relative contribution of each gaseous effluent has also been calculated. The five major aldehydes emitted by vehicles in the tunnel are formaldehyde, acetaldehyde, butanal, propanal and acrolein. Their average relative contributions with the standard deviation indicated in brackets are respectively 34.3% (4.6%), 18% (2.3%), 17.4% (5.7%), 14.5% (6.6%) and 7.8% (4.1%).

Table 3   Average NO_2 concentration during summer 2007 with loaded measurement systems and diffusive bodies in upward and downward tubes (unit: $\mu g/m^3$)

	Upward tube		Downward tube	
	Moving vehicle measurement[a]	This study	Moving vehicle measurement[a]	This study
NO	1600		240	
NO_2	430	169/241	230	69
NOx	2030		470	
Sampling : duration (sec)	133	10600	193	10600
Number	50	9	50	9

The values in the third column represent respectively the NO_2 concentration in UA (middle upward location) and UC (exit upward location).
[a] Morin et al., 2007.
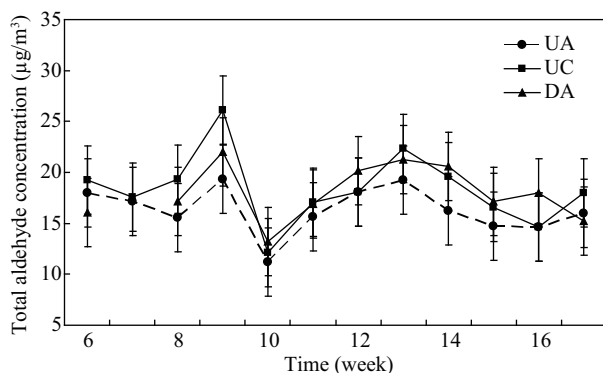
Fig. 5 Total aldehyde concentration evolution (winter period). UA, UC and DA represent respectively the three sampling locations: middle position, exit position in upward tube and middle position in downward way. Winter 2009 sampling period: week numbers 5–17. Error bars: standard deviation.

Table 4 Average aldehyde concentration with the standard deviation obtained during the winter campaign at all sampling locations ($\mu g/m^3$)

	UA	UC	DA
Formaldehyde	5.40 ± 0.53	6.05 ± 1.00	6.38 ± 0.65
Acetaldehyde	2.87 ± 0.46	3.11 ± 0.60	3.48 ± 0.52
Acrolein	1.59 ± 0.95	1.30 ± 0.80	1.22 ± 0.53
Propanal	2.39 ± 1.21	2.38 ± 1.31	2.82 ± 1.20
Butanal	2.70 ± 1.24	3.73 ± 2.01	3.08 ± 1.22
Benzaldehyde	0.10 ± 0.14	0.07 ± 0.11	0.08 ± 0.13
Isopentanal	0.07 ± 0.14	0.18 ± 0.21	0.07 ± 0.11
Pentanal	0.87 ± 0.21	1.13 ± 0.48	0.57 ± 0.17
Hexanal	0.31 ± 0.31	0.43 ± 0.44	0.27 ± 0.36
Total of aldehydes	16.3	18.38	17.97

They represent 90% to 95% of the total aldehyde emission. The formaldehyde emission forms around 34% of the total aldehyde emission independently of the location in the tunnel. The ratio of average formaldehyde/acetaldehyde, formaldehyde/propanal, formaldehyde/butanal concentrations vary respectively between 1.8–1.94, 2.26–2.5 and 1.62–2.09. We can notice a factor two between formaldehyde emission and the other abundant species. Our results about formaldehyde, acetaldehyde and benzaldehyde emission concentrations are two to four times lower than those indicated by Ho et al. (2007). The average density (ca. 53300 vehicles per day) crossing the Hong Kong tunnel and the composition of the vehicle fleet (45% diesel fuelled vehicles) can explain these differences. Higher carbonyl emissions were found to be associated with a high proportion of diesel fuelled vehicles (Ho et al., 2007). An even stronger dependence with heavy duty diesel vehicles is observed by Kristensson et al. (2004) for the five major aldehydes mentioned in our study and others as acetone, crotonaldehyde, toluaaldehyde, hexanal. So larger amount of aldehydes and ketones is emitted by the heavy duty vehicles, compared to gasoline powered cars.

Different studies about aldehydes and especially formaldehyde and acetaldehyde emission factors have been made in some tunnels for any kind of vehicles but also according to engine types (diesel/gasoline) or vehicle types such as light duty or heavy duty vehicles (Table 5). Calculated formaldehyde EF in the tunnel is

lower than those obtained by Staehelin et al. (1998), Grosjean et al. (2001) and Kristensson et al. (2004). EF of the second abundant gaseous effluent, acetaldehyde, remains lower than the values obtained by Staehelin et al. (1998), Grosjean et al. (2001) and Kristensson et al. (2004). Acrolein and propanal EF are in accordance with those obtained by Staehelin et al. (1998) and Kristensson et al. (2004) while benzaldehyde EF value is lower than those published. In our study, benzaldehyde emission represents only 0.4% of the total aldehyde emission. No EF values are indicated in the literature for the other aldehydes. Grosjean et al. (2001) report that the total number of vehicles, the fleet composition, the fleet age, the average speed and the number of vehicles that may be high emitters of carbonyl compounds can influence carbonyls emissions. Over the period 1994–1999, the observations made in Caldecott tunnel show a reduction of emission factor values of 50% for formaldehyde, 47% for acetaldehyde and 71% for benzaldehyde. These reductions include the combined effect of fuel changes and fleet turnover (Kean et al., 2001). Several possibilities may explain that our values are lower than previous studies. This period of 8–14 years between our study and those mentioned above was a period of change both in terms of engine improvements, spread of catalytic technologies, fleet turnover and regulatory developments of fuel. Notice also that the traffic density and speed limit of vehicles are lower in comparison with the others studies. Finally, the sampling conditions, namely 1-hr or 2-hr sampling period, chosen by Kristensson et al. (2004), Staehelin et al. (1998) and Grosjean et al. (2001) are quite different from our sampling period (168-hr) that includes all traffic situations (morning or afternoon traffic and rush-hour traffic peaks, constant traffic and low-density week end and night traffic). Values obtained can be lower or at most equal to those given in the studies previously mentioned.

2.5 BTEX concentration

Figure 6 shows the evolution of total BTEX concentration (the sum of the concentrations of benzene, toluene, ethylbenzene and xylene) according to time during the two sampling periods. In continuity with the previous results, whatever the sampling period, the results indicate a higher concentration at the exit of the bore than in the middle of the tunnel in the ascending tube, and also a higher value in the ascending way than in the descending way. We find again a pumping effect similar to that observed for the NO₂ concentration.

As previously, the average concentration and standard deviation are calculated and summarized in Table 6 for each sampling position. As regards the BTEX, the total concentration is higher in summer as usually observed with higher temperatures. The summer/winter ratio of the total BTEX concentration is unchanged whatever the sampling stations. The summer/winter ratio of each BTEX pollutant is summarized in Table 7. This ratio remains constant in the tunnel but changes with the type of observed effluent (ethylbenzene > toluene > xylene). Only the summer/winter ratio of benzene varies significantly

Table 5   Comparison of aldehyde emission factors in different tunnel studies (unit: mg/(km·veh))

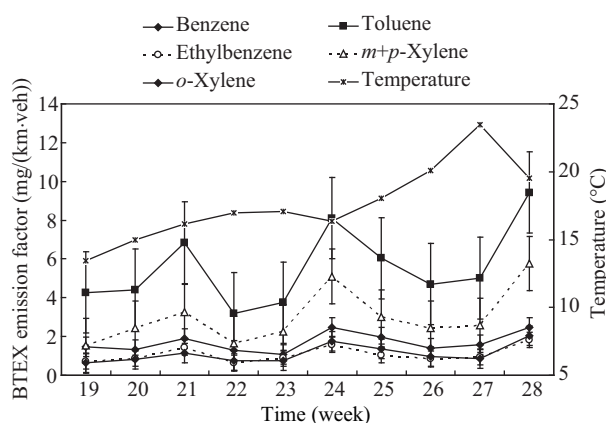|	Grand Mare Tunnel Winter This study	Söderleds Tunnel Winter 95/96 (Johansson et al., 1997)	Söderleds Tunnel Winter 98/99 (Kristensson et al., 2004)	Tingstad Tunnel Winter 94/95 (Kristensson et al., 2004)	Shing Mun Tunnel 2004 (Ho et al., 2007)	Van Nuys Tunnel 93 (Fraser et al., 1998)	Tuscarora Tunnel 99 (Grosjean et al., 2001)	Grubist Tunnel 93 (Staehelin et al., 1998)
				Overall fleet				Gasoline vehicle
Upward bore								
Formaldehyde	1.87 ± 1.05*	18 ± 3	13 ± 3*	20	18.8 ± 7.5	20.3*	5.41	10.54 ± 8.06
Acetaldehyde	0.98 ± 0.47*	28 ± 8	3.1 ± 0.8		5.5 ± 2.2	4.6	2.19	2.33 ± 1.12
Acrolein	1.45 ± 3.90*				0.4 ± 0.3			1.29 ± 0.35
Propanal	0.41 ± 0.35*		0.47 ± 0.2					0.18 ± 0.45
Butanal	1.15 ± 0.60*							
Benzaldehyde	0.07 ± 0.10*	9.5 ± 0.7	3.8 ± 0.7		1.0 ± 0.7	3.2	0.44	
Isopentanal	0.32 ± 0.28*							
Pentanal	0.91 ± 0.69*							
Hexanal	0.92 ± 1.05*							

* Values represent the 95% confidence intervals of each EF calculated in this study.
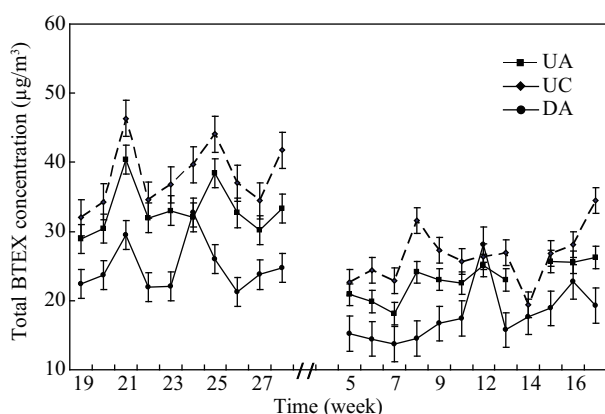
Fig. 6   Total BTEX concentration evolution during summer and winter period at the three sampling locations. Summer 2007 campaign: week numbers 19–28 and winter 2009 sampling period: week numbers 5–17. Error bars: standard deviation.

Fig. 7   BTEX emission factor (EF) evolution during. Error bars: ± standard deviation.

between the two bores. The toluene/benzene concentration ratio calculated in summer and winter (Table 6) remains unchanged for all locations respectively in summer and winter. Toluene is considered as a precursor of benzaldehyde. In our study, the concentration of benzaldehyde is low and represents 0.4% of total aldehyde emission as mentioned previously. It is unlikely that this reaction from toluene to benzaldehyde significantly changes the concentration of toluene. Volatility of toluene and benzene differs depending on temperature and the difference between the vapour pressure of toluene and benzene decreases slightly with increasing temperature in the range of temperature measured in this study. Hence, this toluene/benzene ratio is smaller in winter than in summer.

Emission factors have been also calculated in the ascending tube and summarized in Table 8 with the results from literature data. The values obtained in summer or winter give the same rough estimate. The comparison with the recent studies issued shows that our results are lightly smaller than those published for the Grubist tunnel study (Stemmler et al., 2005) and clearly lower than the values measured in Tapei tunnel (Hwa et al., 2002). Figure 7 shows the evolution of emission factors EF according to time in summer. EF variation of BTEX effluents is linked to the temperature (Fig. 7), showing a clear increase for

the main ones, i.e., toluene and xylene, each time the temperature increases.

3 Discussion

This study in the Grand Mare tunnel defines the real conditions of material exposition and highlights the presence of specific gaseous effluents such as NO_2, SO_2, BTEX and the five major aldehydes, i.e. formaldehyde, acetaldehyde, propanal, butanal and acrolein in this semi enclosed environment. This atmosphere is complicated by the large number of gaseous effluents having an effect on material corrosion. Therefore, understanding the impact of these gaseous pollutants on the degradation of materials is difficult without the knowledge of the action of each pollutant considered individually. Thus, laboratory studies under carefully controlled conditions have been made to identify the effect of each pollutant and to investigate the synergetic effect of the combination of effluents. Studies have been conducted on various materials such as copper, nickel or zinc in different environments with varying concentrations of pollutants tested, relative humidity and temperature. Table 9 summarizes the experimental conditions listed from the literature as well as the impact of effluent on the corrosion rate. From this survey we can extract some interesting pieces of information. The effect of an NO_2-

Table 6 Average BTEX concentration during the two campaigns at all sampling locations and the total BTEX summer/winter concentrations and toluene/benzene ratios (unit: μg/m³)

	Middle upward tube UA			Exit upward tube UC			Middle downward tube DA		
	Summer	Winter	Ratio S/W	Summer	Winter	Ratio S/W	Summer	Winter	Ratio S/W
Benzene	4.1 ± 0.3	3.1 ± 0.2		4.8 ± 0.4	3.5 ± 0.5		2.9 ± 0.3	2.4 ± 0.4	
Toluene	15.4 ± 1.6	10.3 ± 1.5		17.6 ± 2.1	11.8 ± 2.0		11.7 ± 1.7	8.0 ± 2.0	
Ethylbenzene	2.9 ± 0.4	1.7 ± 0.2		3.3 ± 0.5	2.0 ± 0.3		2.2 ± 0.4	1.3 ± 0.3	
m+p-Xylene	7.8 ± 1.1	5.9 ± 0.7		9.0 ± 1.5	6.7 ± 1.1		5.8 ± 1.0	4.5 ± 1.1	
o-Xylene	3.0 ± 0.4	2.1 ± 0.2		3.4 ± 0.6	2.4 ± 0.4		2.2 ± 0.4	1.6 ± 0.4	
Total of BTEX	33.2	23.1	1.44	38.1	26.4	1.44	24.8	17.8	1.39
Toluene/Benzene	3.76	3.33		3.70	3.37		3.99	3.29	

Table 7 Summer/winter average concentration ratios of each BTEX

	Benzene	Toluene	Ethylbenzene	*m+p*-Xylene	*o*-Xylene
Middle upward tube - UA	1.30	1.47	1.66	1.31	1.37
Exit upward tube - UC	1.34	1.47	1.67	1.33	1.39
Middle downward tube - DA	1.19	1.44	1.61	1.27	1.33

Table 8 Comparison of BTEX emission factors in different tunnel studies (unit: mg/(km·veh))

	Benzene	Toluene	Ethylbenzene	*m+p*-Xylene	*o*-Xylene	1,2,4-Trimeth benzen	References
All vehicle	1.69 ± 0.35*	5.58 ± 1.43*	1.07 ± 0.28*	3.00 ± 1.00*	1.10 ± 0.33*		Tunnel Grand Mare summer 2007 (This study)
All vehicle	1.75 ± 1.00*	6.16 ± 3.64*	1.00 ± 0.60*	3.40 ± 2.05*	1.19 ± 0.75*		TunneL Grand Mare winter 2007 (This study)
Average	20.6 ± 1.7	76.5 ± 5.9					Söderleds Tunnel Winter 95/96 (Johanson et al., 1997)
Average	17.3 ± 0.3	67.3 ± 1		48.6 ± 0.8	19.6 ± 0.4		Söderleds Tunnel Winter 98/99 (Kristensson et al., 2004)
Average	52 ± 9	120 ± 21	22	65	24		Tingstad Tunnel Winter 94/95 (Kristensson et al., 2004)
All vehicle	13.69	26.27	4.29	15.49	7.76	7.8	Grubist Tunnel Sept 93 (Staehelin et al., 1995)
All vehicle	2.7 ± 0.3	6.4 ± 0.8	1.4 ± 0.2	4.0 ± 0.5	1.8 ± 0.2		Grubist Tunnel 2002 (Staehelin et al., 2005)
All vehicle	7.9 ± 2	16.9 ± 4.8	3.6 ± 1	12.1 ± 3.6	5.7 ± 1.5		Tauern Tunnel 97 (Schmid et al., 2001)
All vehicle	101 ± 10	173 ± 17	26.4 ± 1.6	88 ± 6.6	33 ± 1.7		Tapei Tunnel 88 (Schmid et al. ,2001)
All vehicle	12.21 ± 3.26	29.02 ± 4.95	5.88 ± 1.55	8.95 ± 2.38	7.88 ± 2.14	14.28 ± 2.94	Tapei tunnel 2002 (Hwa et al., 2002)

* Values represent the 95% confidence intervals of each EF calculated in this study.

polluted atmosphere on the degradation of metals depends on relative humidity, temperature and on the composition of the materials tested: it has no impact on zinc, and has an effect on nickel and copper at low RH. In an SO₂-polluted atmosphere, a small effect on the corrosion of copper or nickel is observed. By contrast, the zinc substrate is deteriorated significantly and SO₂ and relative humidity have therefore an accelerating effect. In an O₃-polluted atmosphere, no effect is observed independently of the materials tested. However it is important to notice that ozone as well as NO₂ have a synergistic effect in a mixed atmosphere (SO₂ + NO₂) or (SO₂ + O₃). This effect is more or less important depending on the experimental conditions. A significant corrosion rate for copper or a dramatic deterioration of zinc substrates is observed in an (SO₂ + O₃) environment. Ozone increases the rate of deposition of SO₂. This rate increases when the concentration of SO₂ decreases. One of the actions of ozone is to promote the oxidation of S(IV) to S(VI). In a mixed atmosphere (SO₂ + NO₂), the synergistic accelerating effect of NO₂ on the corrosion kinetic of zinc substrates depends on relative humidity. In the case of nickel, NO₂ accelerates SO₂-induced corrosion significantly more than O₃. As regards copper, a clear synergistic effect is observed when [NO₂] is higher than [SO₂] in the presence of moisture.

The accelerating effect of NO₂ appears indirectly by an increase in the rate of oxidation of SO₂ to sulfates by a catalytic surface reaction. The relative humidity also plays a fundamental role in the interaction of NO₂ and SO₂ gases with the surface of materials, inducing a number of increasing water monolayers, 1–10 in the range 25%–95% RH (Phipps et al., 1979).

The concentration of SO₂, measured in the tunnel, ranges from 1 to 13 μg/m³, lower values than those used for accelerated laboratory tests. At the centre of the tunnel, NO₂ values in the ascending and descending lanes are respectively 170 and 70 μg/m³. The concentration ratio of NO₂/SO₂ being at least greater than 12, the mixed atmosphere (SO₂ + NO₂) is expected to have a clear synergistic effect especially above critical RH, *T* couple values with 95%–99% RH in winter and around 35%–40% in summer. For such a high ratio, the impact of NO₂ alone on the corrosion process will be expected to be significant in low relative humidity atmospheres. Ozone is not emitted directly in the air but appears as the result of photochemical reactions that involve VOCs and NO*x* as precursors. Hwa et al. (2002) have determined the main VOCs and their reactivity to contribute to ozone formation. The ozone formation potential was calculated from emission factors and on the basis of 100 mg VOCs emitted. In our study, it is unlikely that BTEX are involved in ozone formation because of our comparatively low values of emission factor and because of the difficulty to achieve photochemical reactions. It is also known that carbonyl compounds (especially formaldehyde and acetaldehyde) are significant precursors for ozone formation (Guo et

Table 9   Experimental conditions of laboratory studies mentioned in literature

Experimental conditions	Mariaca et al. (2008)	Zakipour et al. (1997)	Zakipour et al. (1995)	Stranberg et al. (1997)	Svedung et al. (1983)	Svensonn et al. (1993)	Castano et al. (2007)
RH %	50, 70, 90	75	75	70; 90	40–80	70; 95	70; 90
Temp. (°C)	15, 25, 35	22	25	–		22	25; 35
SO_2 (µg/m^3)	200; 800	70.5; 141; 282	28.2; 56.4; 141	169; 1340	169	635	800
NO_2 (µg/m^3)	200; 800	50.6; 101; 203	506	–	101	810	800
O_3 (µg/m^3)	–	52.8; 106; 211	21.1; 42.3; 528	190; 1060		845	
$SO_2 + NO_2$			316 – 506				
$SO_2 + O_3$	–		316 – 528				
Substrate	Cu	Ni	Cu	Cu	Gold coated CuZn	Zn	Zn
Impact with regard to corrosion rate	**NO_2 alone** 1. Effect depends on RH value 2. Low RH: Corrosion most high **SO_2 alone** 1. Low corrosion effect 2. RH : no influence 3. Attack rising with time **$SO_2 + NO_2$** Synergistic effect clear as $[NO_2] > [SO_2]$	**SO_2** No difference with "pure air atmosphere" **NO_2; O_3 alone** 1. Corrosion effect higher for NO_2 than O_3 2. Corrosion effect rising with O_3 concentration **Mixed atmosphere** Corrosion effect significantly more higher for $SO_2 + NO_2$ than $SO_2 + O_3$	**$SO_2 + NO_2$** 1. No corrosion effect 2. Synergistic effect more important as RH > 75% **$SO_2 + O_3$** Important corrosion rate	**O_3 alone** No effect **SO_2 alone** Effect varying with RH value **$SO_2 + O_3$** Important corrosion rate	**NO_2 alone** Corrosion attack when RH > 40% **SO_2 alone** Aggressive pollutant when RH > 60 % **$SO_2 + NO_2$** Favorised an sulphuric acid layer	**O_3 alone** Effect negligible **NO_2 alone** Effect negligible **SO_2 alone** Powerful corrosion accelerator as function of RH **$SO_2 + NO_2$** Acceleration of corrosion at high RH **$SO_2 + O_3$** Increase of corrosion rate dramatically	**NO_2 alone** Very little corrosion for two RH and Temperature **SO_2 alone** 1. Kinetic of corrosion at high RH 2. Effect negligible at RH : 70% 3. Corrosion rate increasing with time **$SO_2 + NO_2$** 1. Great corrosion 2. Synergistic effect as fuction of RH

al., 2004). Formaldehyde and acetaldehyde are known to be very volatile and soluble in water in our exposure conditions with high relative humidity. They form formic and acetic acid available in the electrolyte covering the material surface. It turns out that the ozone concentration, measured in the tunnel, is around the detection limit as a result of low photochemical reactions and (or) ozone consumption during the oxidation of S(IV) to S(VI).

Few studies have investigated the impact of formaldehyde or acetaldehyde on the corrosion of metallic materials. Corrosion products such as formate or acetate are found on sensitive items displayed in museum enclosures contaminated with acetic or formic acid vapours. Metallic items are also sensitive to organic attack, lead being one of the most cited cases (Niklasson et al., 2008). Laboratory studies were recently conducted to determine the impact of acetic acid vapours on lead substrate (Niklasson et al., 2008) and formic acid vapours on copper, brass and lead (Gibson et al., 2010). In both cases, an accelerating effect was found. The corrosion rate is weakly dependant on relative humidity in the range of 50%–95% RH with respect to acetic acid. Singh et al. (1995) have studied the corrosion of copper in aqueous solutions of formic or acetic acids. Their results indicate that formic acid is more corrosive than acetic acid. The organic acids, considered to be weak acids, provide sufficient protons to act as true acid toward metals. Despite much lower concentrations than those used in the laboratory tests (449 µg/m^3, 2908

µg/m^3 for CH_3COOH (Niklasson et al., 2008) and 100 mg/m^3 for $HCOOH$ (Gibson et al., 2010)), formaldehyde and acetaldehyde may have an impact on the degradation of materials as well as the other two dominant aldehydes (butanal and propanal). Butanal oxidizes in the air to form butyric acid, soluble in water. In the electrolyte, it can be oxidized by sulphuric acid and form CO_2 and acetic acid, corrosion accelerator as mentioned above. In the same way, butanal and propanal can form propanoic acid with a corrosive effect on some materials (Baah, 1996).

As a guide, the values of the main pollutants studied above near the heavy traffic road during the same winter period (sampling height: 3 m; distance of traffic line: 5 m) are respectively NO_2 (52 µg/m^3), benzene (2 µg/m^3), toluene (6.6 µg/m^3), ethylbenzene (1 µg/m^3), $m + p$-xylene (3.8 µg/m^3), o-xylene (1.4 µg/m^3), formaldehyde (3 µg/m^3) and acetaldehyde (1.4 µg/m^3).

It is worth noting that a lot of factors affect the gaseous pollutants amount emitted by automobile such as vehicle fleet, motor improvement, catalytic technology and type of fuel. During the interval of two years between the two campaigns the composition of the fuel has not undergone specific change (regulation EN 228:2004). The motor improvement and the catalytic technology are closely linked. During this period, the new vehicles in circulation had to respect the regulation EURO3 then EURO4 from 2005. The fleet turnover takes place over a period of 5 to 6 years. Our results show that traffic fleet remains constant.

4 Conclusions

This work presents the atmosphere generated by road traffic in an urban tunnel in upper Normandy, France. SO_2, NO_2 and BTEX concentrations are significantly higher in the ascending tube than in the descending one. The aldehyde concentration profiles do not present a clear difference between the two tubes.

Emission factors values of the main pollutants are, on the whole, in accordance with the data published in literature. This work presents also for the first time the emission factor values of some gaseous effluents. This atmospheric study is the preliminary step of a research programme on the impact of road traffic on the degradation of materials in a semi-confined environment. The relative humidity prevailing in the tunnel will also play a key role in the degradation process. Among the identified pollutants, SO_2 and NO_2 are important factors of the corrosion process. The mixed atmosphere ($SO_2 + NO_2$) will have a synergistic effect on the corrosion of materials. NO_2 concentration is directly linked to change in the automotive flow. The five dominant aldehydes emitted by automotive traffic, i.e., formaldehyde, acetaldehyde, butanal, propanal and acrolein – representing 90% to 95% of the total aldehyde emissions, will also have an accelerating effect on corrosion. Regarding BTEX considered as precursors of ozone formation, we can expect a negligible impact.

Acknowledgments

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