

The impact of NO_x, CO and VOC emissions on the air quality of Zurich airport

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Abstract

To study the impact of emissions at an airport on local air quality, a measurement campaign at the Zurich airport was performed from 30 June 2004 to 15 July 2004. Measurements of NO, NO₂, CO and CO₂ were conducted with open path devices to determine real in-use emission indices of aircraft during idling. Additionally, air samples were taken to analyse the mixing ratios of volatile organic compounds (VOC). Temporal variations of VOC mixing ratios on the airport were investigated, while other air samples were taken in the plume of an aircraft during engine ignition. CO concentrations in the vicinity of the terminals were found to be highly dependent on aircraft movement, whereas NO concentrations were dominated by emissions from ground support vehicles. The measured emission indices for aircraft showed a strong dependence upon engine type. Our work also revealed differences from emission indices published in the emission data base of the International Civil Aviation Organisation. Among the VOC, reactive C₂–C₃ alkenes were found in significant amounts in the exhaust of an engine compared to ambient levels. Also, isoprene, a VOC commonly associated with biogenic emissions, was found in the exhaust, however it was not detected in refuelling emissions. The benzene to toluene ratio was used to discriminate exhaust from refuelling emission. In refuelling emissions, a ratio well below 1 was found, while for exhaust this ratio was usually about 1.7.

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1. Introduction

The impact of air traffic on the atmosphere has been the subject of several studies in recent years. An

overview is given in Rogers et al. (2002). However, compared to the number of studies focusing on the aeronautic impact to the upper troposphere and lower stratosphere (Brasseur et al., 1998), only a small fraction of the research has evaluated local air quality at airports. Though routine in-situ measurements of carbon monoxide (CO), nitrogen monoxide (NO), nitrogen oxides (NO_x) and other compounds, as well

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as path-integrated measurements by differential optical absorption spectroscopy (DOAS) of NO and nitrogen dioxide (NO₂), are performed by airport authorities and usually published in annual environmental reports, some important open questions about airport air quality remain unanswered. Two of these questions are addressed in this work. The first question is, “What are typical speciations for volatile organic compounds (VOCs) of engine exhaust and kerosene refuelling” and the second question is, “Do real in-use emissions of NO_x and CO correspond to those values used in emission inventories?” The answers to these questions are essential for a better understanding of air quality at airports.

The determination of VOCs related to aircraft activities, during different engine operation levels, has been the subject of a few studies. Spicer et al. (1992, 1994) investigated military and civil jet engines in a test bed. Scherer (1996) focused on VOC in a medium volatility range in a test bed study, as well as in a field study in the vicinity of the airport Zurich–Kloten, Switzerland, to determine the influence of the airport on local air quality. Despite these works, no compound was found that could serve as a tracer for engine exhaust (Tesseraux, 2004). VOC emissions related to aircraft are not only emitted during combustions, but also result from resting losses from aircraft fuel tanks, during the refuelling of an aircraft. Usually, aircraft are refuelled shortly after arrival. In this case, the airframe structure is still quite cold and there is only a moderate fuel–air-mix in the tanks. During refuelling, however, the gaseous air–fuel mixture is released through the fuel vents of the aircraft tanks which are most often located in the wings. Emissions of this type are of the order of 2.7% of the total VOC emissions of the Zurich airport. Hot soak emissions from the shut down of aircraft main engines are small. Experts of the CAEP alternative emission methodology task group (AEMTG) believe that the actual HC emissions can be neglected in comparison to emissions produced during the standard landing and takeoff (LTO) cycle.

During approval of a new engine by the International Civil Aviation Organization (ICAO), engine emissions of NO_x and CO are measured in a test bed for four different thrust settings: Idle (7% of maximum thrust), approach (30%), climb out (85%) and take off (100%).¹ Usual emission

characteristics show high CO and low NO_x emissions during low thrust conditions due to incomplete combustion. In contrast, during high thrust levels, combustion is nearly complete and the temperature in the engine reaches maximum values leading to high NO_x and low CO emissions. ICAO's idling emissions (at 7% of maximum thrust) represents a mean emission of the aircraft on the whole airport and therefore it is a mixture of true idling and taxiing. Due to the lower thrust of real idling, CO emissions will be even higher, and NO_x emissions lower than those provided by the ICAO. These emission indices are widely used in emission models for airports, but little work has been done so far to test these indices under real in-use conditions. Popp et al. (1999) and Herndon et al. (2004) estimated NO and NO_x emission indices for different thrust levels but compared only few engines with ICAO data. Schäfer et al. (2003) did this comparison systematically for idle thrust and found differences between measured and certificated values. NO_x emission indices were usually about 50% lower than those provided by ICAO, while CO emission indices were slightly higher, because thrust settings were usually lower than those defined by ICAO for idling.

Other emissions emanating from the airport environment occur during the handling of aircraft. Ground support equipment (GSE) encompasses all vehicles and machinery needed to service the aircraft on the ground between arrival and departure events. The vehicles are mostly diesel powered, therefore, as a result, the main emissions expected from these sources are particulate matter and oxides of nitrogen.

2. Experiment

2.1. Study area and measurement sites

The study area was located between piers A and B of the Zurich airport (Fig. 1). At pier A, up to four aircraft could be parked and simultaneously handled. Pier B was used for long-term parking of aircraft and no handling took place there. Trace gas measurements were carried out at four sites within these areas during 2 weeks in 2004 (30 June 2004–15 July 2004). According to their position, the measurement locations are called “handling”, “taxiway”, “pier B” and “pier A” (Fig. 1). An aircraft that is ready for departure usually undergoes the following steps: The aircraft is pushed back by a

¹Data freely available at <http://www.caa.co.uk/default.aspx?categoryid=702&pagetype=90>.

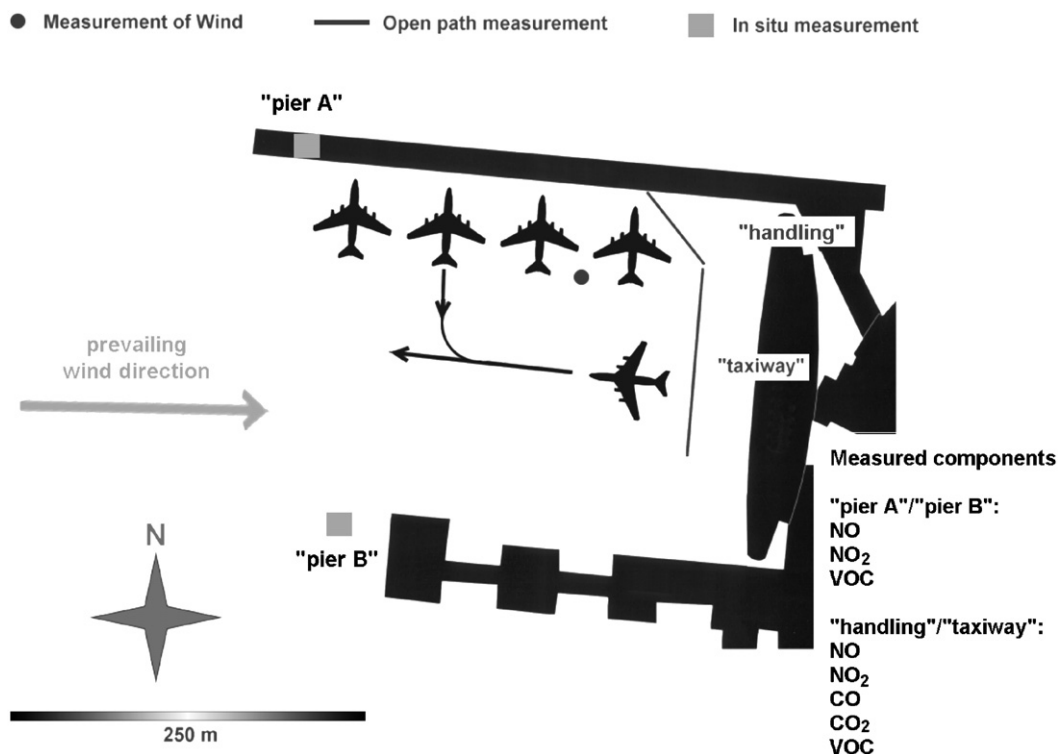


Fig. 1. Schematic of the experimental setup.

tow vehicle onto the taxiway and, simultaneously, the engines are ignited. The tow vehicle disengages from the aircraft, the aircraft stands on the taxiway for approximately one minute with idle thrust and the engine exhaust was blown towards the measurement path "taxiway". The aircraft leaves the study area under its own power. Measured components were CO, carbon dioxide (CO₂), NO, NO₂, and VOC. Measurement devices for NO and NO₂ were operated continuously and unattended, while the CO/CO₂-devices needed permanent supervision and were run during daytime only. Air samples were collected into electro-polished stainless steel canisters and later analysed for VOC in the laboratory. VOC canister sampling was done to pursue two different goals. One subset of canisters was used to obtain temporal variations (on 9 July from 1 p.m. until 6 p.m.) of ambient VOC at Piers A and B, whereas another subset of canisters was exclusively taken to retrieve typical VOC fingerprint data for emissions including aircraft exhaust emissions during engine ignition, idling, and taxiing. Samples were taken directly within the plume of the engine, about 50–100 m behind an aircraft, at a height of 1 m. In this case, differing from standard proce-

dures, engines were not ignited until the aircraft was standing on the taxiway. The first sample was taken at the time when the hot air hit the sampling location. This moment was detected by the operators feeling the hot air. It is assumed, that this sample corresponds to aged emissions of engine ignition. The second sample was taken after this phase, i.e. before the aircraft had moved, but with the engines at idle power. As soon as the aircraft began to move, the third sample—taxiing—was taken. Prior to taking a sample, the canisters were flushed twice with ambient air. The filling of the canisters lasted approximately one minute (They were filled up to 2 bar).

Air chemistry data was complemented by wind measurements determined by means of a METEK three-dimensional ultrasonic anemometer which is operated permanently at the airport Zurich-Kloten.

2.2. Open-path measurements

Open-path measurements are based on the physical effect that many trace gases in ambient air and exhaust compounds absorb radiation in the ultraviolet (UV), visible, and infrared spectral

range. Two methods are used in this study: Fourier transform infrared (FTIR) spectroscopy in the infrared and DOAS in the UV/visible spectral range.

The open-path measurement using FTIR spectroscopy consists of an infrared source, at one end of the measurement path, and a spectrometer at the other end. Two FTIR systems were operated in this field study. Path-averaged gas concentrations are determined by the differential absorption method and least squares fitting of measured and reference spectra using a software code from Kayser–Threde (Haus et al., 1994). Spectrometers from Kayser–Threde were used which are equipped with gaseous nitrogen cooled detectors and provide a spectral resolution of up to 0.2 cm^{-1} . The time for one measurement is about 3 min. Fifty interferograms are added during a single measurement to suppress noise. The concentrations of the investigated compounds of this multi-component measurement method are determined simultaneously. The detection limits for a 100 m absorption path length, which is typical for this experiment, are 2 mg m^{-3} for CO_2 and $6\text{ }\mu\text{g m}^{-3}$ for CO. Validations with in situ measurements by canister sampling along the absorption path were performed by Haus et al. (1994) and revealed an uncertainty within ($\pm 5\%$) of the used FTIR system.

NO and NO_2 can be detected in the UV/visible spectral region with higher sensitivities than in the infrared due to greater absorption coefficients; cross-sensitivities with other gases (as water vapour in the infrared) are important. The measurements were performed with a DOAS system from OPSIS AB in mono-static configuration. The emitter/receiver unit of the DOAS system was equipped with a xenon lamp (UV/visible). The different paths and the optical alignment are performed automatically so that an unattended measurement is possible. The measured components and paths are measured consecutively, by the DOAS, leading to measurement gaps in the time series of each pollutant of about 3 min. For a 200 m open absorption path length, typically used during this experiment, the detection limits are $3\text{ }\mu\text{g m}^{-3}$ for NO_2 and $5\text{ }\mu\text{g m}^{-3}$ for NO with an accuracy of 5–10% (OP SIS, 1997).

The absorption paths for both devices were set parallel. The path lengths in Zurich–Kloten were 58 m for the “handling”-measurement and 125 m for the “taxiway”-measurement (see Fig. 1.).

2.3. In-situ NO_x measurement

In situ measurements of NO and NO_2 were performed at two locations—at the end of pier B (AC30 M, Antechnika GmbH) and on the roof of pier A (ML9841, Monitor Labs), the latter being a measurement station permanently maintained by the Zurich–Kloten airport.² Both instruments are chemiluminescence devices equipped with molybdenum converters. Time resolution for the NO_x measurements was half an hour.

2.4. VOC analysis

Samples of ambient air were taken into electro-polished stainless steel canisters and analysed for VOCs and CO in the laboratory using gaschromatographic methods. The sampling time of the canisters was about 1 min. CO mixing ratios in the canisters were determined by a HgO detector after separating CO from other gases on a column packed by molecular sieve 13X (3 cm \times 2.2 mm i.d) according to a method of Seiler et al. (1980). VOCs were analyzed by a gas chromatographic (GC) method of Habram et al. (1998). This method participated successfully in various intercomparisons (Slemr et al., 2002; Volz-Thomas et al., 2002). The set of canisters included six ambient air samples, one calibration canister containing benzene and *n*-butane in nitrogen, and one canister containing 70 VOC compounds in nitrogen for identification purposes. Both canisters were filled from corresponding gas cylinders provided by Messer Griesheim, Krefeld, Germany, and the National Center for Atmospheric Research (NCAR), Boulder CO/USA and were in the range between 0.16 ppbv (*n*-propylbenzene) and 11.30 ppbv (ethane). The quantification of individual VOC species was based on the *n*-butane response factor. The two species, benzene and *n*-butane, were used to check the consistency and stability of the calibration gas itself. Water removal in air samples was done using an empty PFA tube (300 mm \times 0.25 mm i.d) at $-30\text{ }^\circ\text{C}$. Pre-concentration of the sample was accomplished with a Varian sample pre-concentration trap 800 mm \times 2.1 mm i.d) filled with Carbopack[®] BHT and kept at $-120\text{ }^\circ\text{C}$ using liquid nitrogen. The sample was desorbed at 200 ° and injected into the GC (Varian 3600CX) with He as the carrier gas.

²Freely available at <http://www.unique.ch/dokumente/Luftschadstoff-Monitoring.pdf>.

For the separation, two columns run in parallel, were used: C₂–C₄ VOCs were separated by a PLOT column GasPro GSC (17 m × 0.32 mm i.d.; Astec, Whippany NJ, USA); for the separation of C₄–C₉ hydrocarbons a CP-SIL 5 CB column (50 m × 0.25 mm i.d., 1 μm df; 100% Dimethylpolysiloxane, Chrompack, Middelburg, Netherlands) was used. The hydrocarbons of the sample were detected by a flame ionisation detector (FID) that was kept at 250 °C. Precision of this system is less than 0.9% for compounds in the range between 5 and 50 ppbv. For aromatic compounds, the precision for the same concentration range is 1% for benzene and toluene, 2% for ethylbenzene and 3% for the xylenes. Precision decreases with decreasing mixing ratios: about 1% for mixing ratios between 250 pptv and 5 ppb, more than 3% for mixing ratios between 25 and 250 pptv, and approximately 20% for mixing ratios between 10 and 25 pptv. Precision for aromatic compounds increases accordingly. The detection limit is between 10 and 15 pptv for most compounds for a sample of 400 ml.

2.5. Emission index estimation

To determine emission indices of operating aircraft, the same method as in Popp et al. (1999), Schäfer et al. (2003) and Herndon et al. (2004) is used. In case of CO and CO₂ measurements in the aircraft engine plume and in the background air, it is possible to determine aircraft emission indices. The corresponding equation for emission indices (EI) of CO (EI (CO)) is:

$$EI(\text{CO}) = EI(\text{CO}_2) \frac{c_{\text{peak}}(\text{CO}) - c_{\text{base}}(\text{CO})}{c_{\text{peak}}(\text{CO}_2) - c_{\text{base}}(\text{CO}_2)} A(\text{CO}) \quad (1)$$

with EI(CO₂): emission index of CO₂ (3150 g kg⁻¹ from Schäfer et al., 2003), c_{peak} : measured concentration maximum within the aircraft plume, c_{base} : measured mean concentration before and/or after (3–10 min and depending from the emission situation) the passage of the aircraft plume through the path and A(CO) the ratio of molecular masses of CO to CO₂ (0.6364). Eq. (1) was applied for those peak concentrations c_{peak} , which can be assigned to an observed aircraft passage and which exceed the baseline concentration c_{base} by more than the standard deviation of the baseline concentration. This equation is equivalent to a time and path averaged concentration measurement, if the spatial

concentration distribution within the plume is the same for both trace gases. If the distribution is given as $c(x) = c_{\text{peak}}d(x) + c_{\text{base}}$, with $d(x)$ describing the shape of the plume, then the measured concentration is given as:

$$c_{\text{meas}} \propto \int_{x_1}^{x_2} (c_{\text{peak}}d(x) + c_{\text{base}}) dx. \quad (2)$$

Replacing in Eq. (1) the “real” peak concentration c_{peak} with the measured peak concentration c_{meas} , it can easily be seen, that Eq. (1) also holds for averaged concentrations. To apply this method, it is necessary that the concentration c_{base} does not change much compared to concentration c_{peak} .

3. Results

3.1. Results for NO_x, CO and CO₂

The influence of aircraft operations and wind direction on the measured concentrations is given in Fig. 2. CO concentrations on the “taxiway” path are related to aircraft movements on the taxiway, while the “handling” path is almost not influenced by these activities. This is most likely caused by the momentum of the engine exhaust which is directed towards the “taxiway” path and because of this, the engine exhaust doesn’t reach the “handling” path. Therefore it can be assumed, that the “handling path” is not typically influenced by aircraft exhaust. CO concentrations on the “taxiway” path during aircraft activities are almost insensitive to wind direction. Advection of the exhaust is dominated by the jet momentum and not by ambient conditions. The highest NO concentration can be found on the handling path during westerly wind conditions independent of aircraft operations. Therefore, NO concentrations are mainly influenced by ground support activities. Half hourly NO₂ concentrations show no clear dependence on aircraft activities or wind direction, because NO₂ concentrations are dominated by background levels.

An overview of the measured concentrations during the entire field campaign is given in Table 1. While similar concentration levels at “pier A” and “pier B” are observed, an obvious difference between the stations “pier A”/“pier B” and “handling”/“taxiway” during the daytime can be found. This difference is caused by airport operations during daytime. Overnight, when no aircraft operations took place, concentration levels at all measurement locations were quite similar.

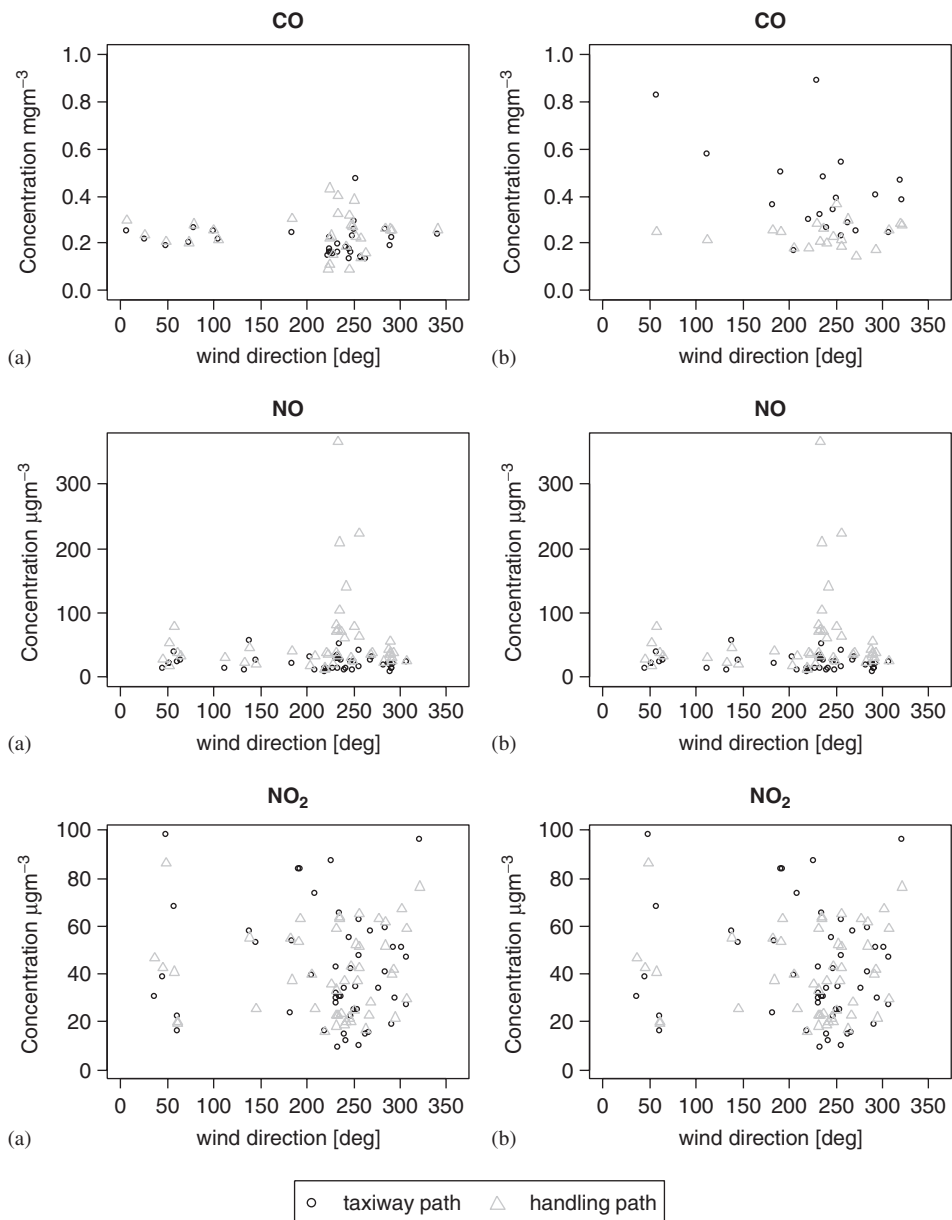


Fig. 2. Half hourly averaged concentrations vs wind direction: (a) Measurements during periods when no aircraft was operating on the taxiway. (b) Measurements during periods when an aircraft was operating on the taxiway.

During the daytime, the prevailing westerly winds transported the emissions towards the measurement paths “handling”/“taxiway” leading to elevated concentrations. This again emphasizes the influence of the investigated area upon the ambient concentration. In particular, significantly higher NO values on the parking lots (“handling”), compared to the taxiway-measurement, were detected. This effect is most likely caused by the relative close vicinity of

the measurement path to moving vehicles with combustion engines. The median of NO₂ concentrations is a little higher on the “handling” path but the maximum values can be observed on the “taxiway” path when the measurement takes place in the plume of the aircraft engine. Regarding these findings, one would assume also high NO peaks related to aircrafts, because previous studies found higher NO concentration than NO₂ at the engine

exit (Spicer et al. 1994; Schäfer et al. 2000). The reason for the conversion of NO to NO₂ might be high O₃ concentrations which occurred during the campaign due to the sunny and warm weather conditions. Similar results have been found by Herndon et al. (2004) in the plume of taxiing aircrafts.

Taking measurement of “pier A”/“pier B” as background measurement ($c_{\text{background}}$) with respect to the measurements in the plume at “handling”/“taxiway” (c_{plume}), one can determine which part of the measured concentrations is caused by the airfield and which part is coming from the background. This influence I is given as:

$$I = \frac{c_{\text{plume}} - c_{\text{background}}}{c_{\text{plume}}} \quad (3)$$

It is found that up to 98% of the NO concentrations are caused by airfield emissions. The mean

influence of the airfield for NO is 56% at the “taxiway” path and 76% at the “handling” path. For NO₂, the maximum influence of the airfield reaches 90%, but the mean values are lower, i.e. 17% for taxiway and 21% for the parking lot (“handling”). This demonstrates the importance of airfield emissions.

CO measurements were only available for the two paths, “handling” and “taxiway”. CO is highly related to aircraft activities on the taxiway (Fig. 3 and Table 1). Each aircraft movement on the taxiway leads to a significant short-term peak of CO. Then the concentration sharply drops back to the background level. The CO baseline varies slightly between 100 and 200 $\mu\text{g m}^{-3}$ during the measurement campaign. Therefore peak concentrations, arising from aircraft emissions, are up to 40 times higher than background concentrations. In some cases CO peaks on the “handling” path have been detected (Fig. 3). These peaks are not

Table 1

Measurement statistics for the entire field experiment (30 June 2004–15 July 2004): For pier A and B, half hourly means of NO_x in situ measurements are shown. For the other two sites FTIR short term data of 3 min resolution are reported. For CO, only daytime measurements were available

	NO ($\mu\text{g m}^{-3}$)			NO ₂ ($\mu\text{g m}^{-3}$)			CO (mg m^{-3})		
	Min	Median	Max	Min	Median	Max	Min	Median	Max
Pier A	bdl	3.1	61.1	3.6	19.6	103.8	—	—	—
Pier B	bdl	6.6	76.3	3.0	17.5	98.3	—	—	—
Taxiway	0.07	15.4	132.0	0.04	22.6	274.0	0.06	0.19	4.49
Handling	0.8	25.2	636.0	0.3	29.6	131.0	0.00	0.22	1.91

bdl: below detection limit of 2 $\mu\text{g m}^{-3}$ for NO₂, 4 $\mu\text{g m}^{-3}$ for NO and 6 $\mu\text{g m}^{-3}$ for CO.

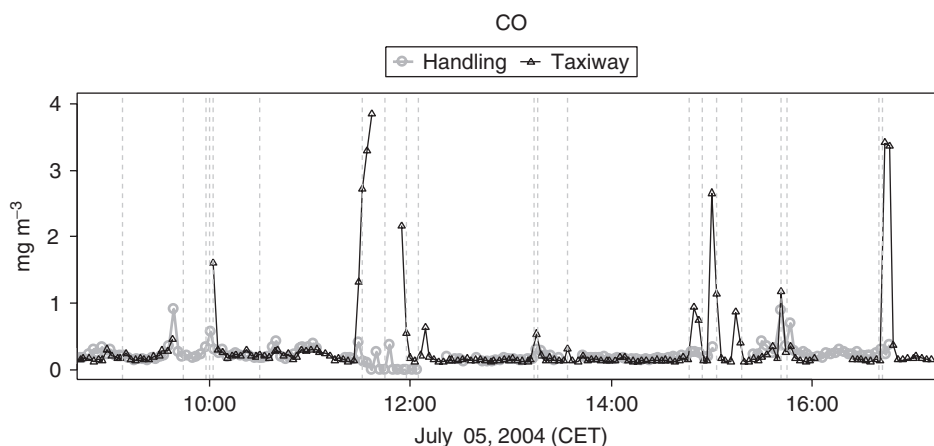


Fig. 3. Time series of CO concentrations at the locations “handling” and “taxiway” (3 min values). Dashed lines denote time when an aircraft moved onto taxiway.

caused by departing aircraft, but by arriving aircraft. Arriving aircraft shut down their engines when they arrive at the stand. The emissions on the stand can be blown towards the handling path (by wind), while departing aircraft ignite engines on their way onto the taxiway and therefore these emissions usually didn't reach the "handling" path.

3.2. Emission indices

CO emission indices were determined for a total of 44 aircraft with eight different engines. An example of concurrent FTIR CO/CO₂ measurement is given in Fig. 4 together with the corresponding aircraft registration. The simultaneous occurrence of CO₂ and CO peaks, which were related to aircraft movements, allowed the calculation of the emission indices for a specific aircraft. A comparison with tabulated emission indices of the ICAO database is given in Fig. 5. The ICAO value lies in between the measured ones. The measurements of the same engine type show large variability of up to 50 g kg⁻¹. The reason for this is most likely due to different thrust settings during idling which causes different emissions. One would expect that real CO emission indices are higher, than the ones by ICAO, because of the lower thrust settings. Most likely this behaviour was not found due to the relative high thrust that is needed to begin taxiing and hence leading again to lower CO emission indices.

3.3. Results for VOC

Airport background VOC values differ from the rural air samples (e.g. sample taken at IMK-IFU, Garmisch-Partenkirchen, Germany, given in Table 2) and are characterised by slightly enhanced values of ethene, ethine, propane, propene, butane, and *i*-pentane. Those species reflect the residual VOC mixture of aircraft and vehicle exhaust (ethene, ethine, propene) and fuel constituents (propane, butane, *i*-pentane). While the rural air sample features a benzene:toluene ratio greater than 1 and thus reflecting photochemically aged air, the airport background air shows a ratio of 1:3 which is representative of mixture of traffic exhaust and kerosene evaporation. It is important to note that in air of Garmisch-Partenkirchen isoprene was found to be at about 1.6 ppbv, whereas at the Zurich-Kloten airport background air showed rather low isoprene values (36 pptv). However, under the influence of aircraft emissions, isoprene values reached a maximum of up to 2.8 ppbv.

Table 2 reports results from VOC samples taken in ambient air at the three sites: pier A, pier B, and the parking lot ("handling") on 9 July 2004 at three selected times. Occasionally, pronounced concentration maxima were observed. For instance, at the parking lot ("handling") location, a refueling of an aircraft nearby was investigated at 17:39. The detailed results show a typical enhancement of *i*-pentane, aromatics and C₂–C₉ unbranched alkanes. No enhancement of high volatile C₂–C₃ alkenes or

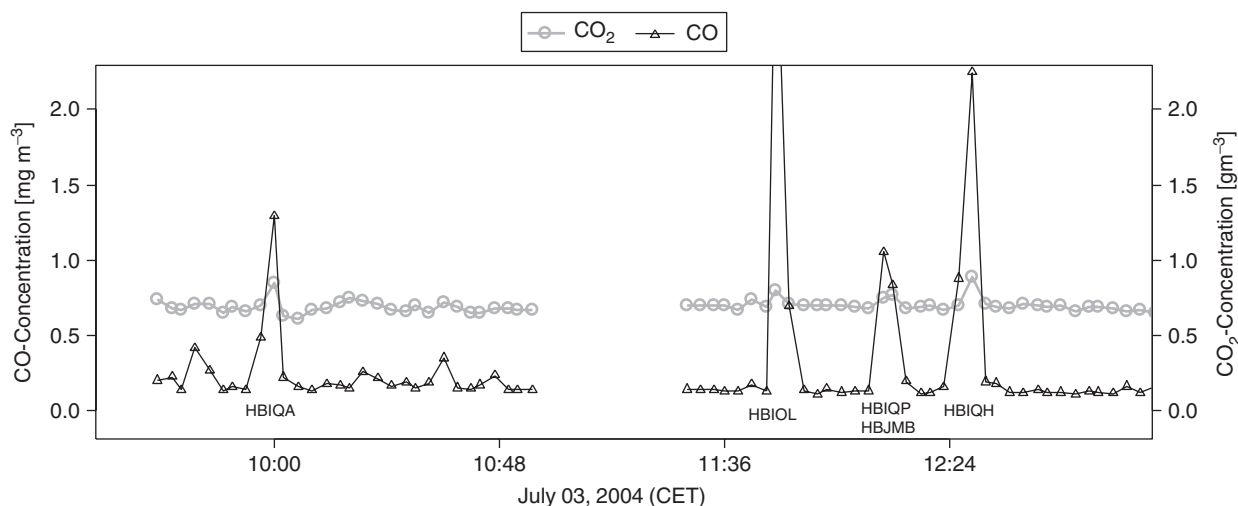


Fig. 4. Time series of CO and CO₂ concentration measurements on the taxiway path. Aircrafts on the taxiway are denoted by their registration code.

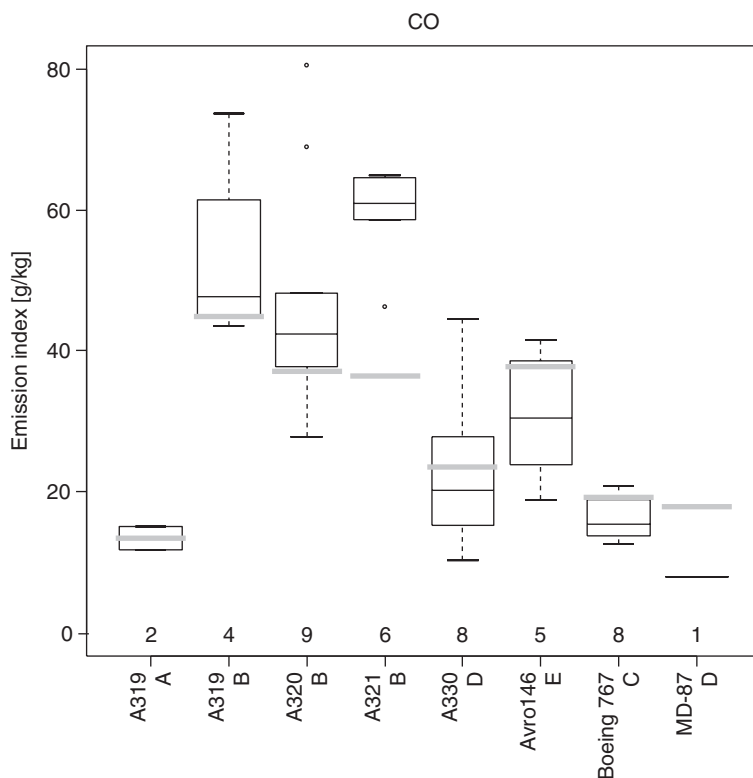


Fig. 5. Emission indices estimated by open-path measurements and comparison to ICAO database. The tabulated emission index of ICAO for idle conditions is given as a grey horizontal bar. The letter adjacent to each aircraft type denotes a specific class of engines. Additionally, the number of observations for each aircraft type is given. Horizontal lines have from bottom to top the meaning of: minimum, 1st quartile, median, second quartile, maximum. Dots stand for outliers as they have been calculated by the software R (R Development Core Team, 2004).

ethine, species related to exhaust, is observed. The benzene:toluene ratio is about 0.27, a typical value for kerosene fuel. Contrary to the aforementioned VOC samples taken in the plume of the aircraft, isoprene has been found at background values in this ambient air sample, which reflects the impact of unburnt kerosene fuel. This result indicates that isoprene is not present in the fuel, but obviously being formed in the kerosene combustion process.

The maxima at pier A (15:05) and B (15:51) show a somehow similar VOC split, however in both cases, the emission source is unknown. There was no aircraft exhaust influence upon the sampling which is clearly reflected in the ethene, ethine, and propene values which are close to background values. While at 15:51 on 9 July 2004, slightly enhanced values C_4 -butanes, C_5 -pentanes, and toluene are observed at pier B, these species are tremendously enhanced at 15:05 at pier A. Also, other VOCs show higher values, but apart from C_4 and C_5 alkenes, these are mainly alkanes up to C_8 .

Results of ambient air sample analyses without aircraft exhaust influence (background) and within aircraft exhaust plumes are given in Table 3. The total VOC (TVOC) mixing ratios in ppbv are also given for each sample. Table 3 shows that VOC compositions vary with type of engine and engine status. Compared to the background measurements, tremendous amounts of highly reactive ethene and propene are emitted. Assuming that cases with high TVOC are least superimposed by other sources, but reflect at best the current engine power, three cases can be identified: taxiing for the HB-IPV engine (TVOC: 780,608 pptv), ignition for the N69154 engine (TVOC: 603,916 pptv), and idle for the HB-IQH engine (TVOC: 782,474 pptv). Typically, in the case of ignition, some high volatile alkanes are enhanced, e.g. propane, butane, *i*-pentane, and pentane, as well as higher aromatics such as toluene, xylenes and styrene. This indicates that during this engine status, the engine has not yet reached its final temperature. Thus higher aromatic compounds are

Table 2
CO and VOC mixing ratios (in pptv, unless otherwise noted) in air samples taken at different times during daytime

Location Time Observations	Pier A; 9 July 2004			Parking place; 9 July 2004			Pier B; 9 July 2004			IMK-IFU, Garmisch Rural site
	13:00	15:05	16:22	13:15	15:25	17:39 Re-fuelling of HB-IJS nearby	13:31	15:51	18:12	
CO (ppbv)	130	78	99	142	185	91	97	77	205	134
Ethane	906	765	868	1126	776	917	986	918	1006	1164
Ethene	1037	637	155	1205	541	460	512	239	1626	326
Ethine	455	158	128	748	680	286	334	237	554	211
Propane	189	3039	210	239	165	396	216	287	158	230
Propene	215	743	37	377	174	157	117	78	387	142
<i>i</i> -Butane	30	46,892	50	117	97	400	bdl	732	60	146
Butane	70	98,265	110	227	276	1598	72	1694	82	221
Propine + 1-butene	27	3370	bdl	80	33	56	bdl	131	65	52
1,3-Butadiene	43	138	bdl	63	bdl	bdl	bdl	43	61	42
<i>tr</i> -Butene	bdl	–999,999	bdl	70	34	36	bdl	218	bdl	31
<i>i</i> -Butene	20	19,804	bdl	140	89	96	46	115	54	95
<i>cis</i> -Butene	bdl	12,355	bdl	18	15	55	23	41	12	21
3- <i>M</i> -1-butene	bdl	2707	bdl	bdl	bdl	bdl	bdl	27	bdl	bdl
<i>i</i> -Pentane	169	349,109	253	619	692	2602	171	2118	232	640
1-Pentene	bdl	5740	bdl	18	26	20	26	50	16	bdl
2- <i>M</i> -1-butene	15	11,663	bdl	12	27	46	13	97	12	bdl
Pentane	35	74,343	61	130	132	2654	92	474	67	132
Isoprene	20	802	107	46	21	70	35	91	79	1665
<i>trans</i> -Pentene	bdl	13,192	bdl	20	17	47	18	122	12	23
<i>cis</i> -Pentene	bdl	6760	bdl	bdl	14	25	bdl	72	bdl	bdl
2- <i>M</i> -2-butene	bdl	18,718	bdl	25	27	30	13	169	bdl	27
2,2- <i>DM</i> -butane	35	29,474	40	91	82	172	38	194	60	76
<i>cyc</i> -Pentene	bdl	2251	bdl	bdl	bdl	bdl	bdl	28	bdl	bdl
4 <i>M</i> +3 <i>M</i> -pentene	bdl	853	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
2,3- <i>DM</i> -butane	bdl	6763	bdl	25	15	406	10	51	27	126
<i>cyc</i> -Pentane	bdl	17,700	13	40	35	338	31	118	bdl	51
2- <i>M</i> -pentane	12	65,051	76	126	189	1937	14	366	34	103
3- <i>M</i> -pentane	17	27,375	45	72	80	1390	21	168	37	56
2- <i>M</i> -1-pentene	15	1964	25	15	67	26	27	34	32	15
Hexane	13	16,206	bdl	51	bdl	3765	bdl	139	22	57
<i>c</i> -3-Hexene	bdl	1035	bdl	bdl	bdl	bdl	bdl	15	bdl	bdl
<i>t</i> -2-Hexene	bdl	1553	bdl	bdl	bdl	bdl	bdl	16	bdl	bdl
<i>c</i> -2-Hexene	bdl	768	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
<i>M</i> - <i>cyc</i> -pentane	bdl	8811	20	29	39	2217	bdl	90	15	25
2,4- <i>DM</i> -pentane	bdl	1428	bdl	23	bdl	216	bdl	20	bdl	bdl
Benzene	174	13,124	280	254	198	1163	146	251	190	394
<i>cyc</i> -Hexane	17	3385	20	36	43	2732	32	59	26	97
2- <i>M</i> -hexane	bdl	6423	bdl	17	102	1554	15	68	11	15
2,3- <i>DM</i> -pentane	bdl	2298	bdl	16	58	641	bdl	32	10	bdl
3- <i>M</i> -hexane	20	7011	15	28	40	2025	18	65	18	37
2,2,4- <i>TM</i> -pentane	10	5575	18	33	43	1103	11	93	22	42
Heptane	bdl	5017	14	25	60	5079	14	56	11	24
2,3- <i>DM</i> -2-pentene	46	56	41	bdl	999,999	bdl	21	40	35	59
<i>M</i> - <i>cyc</i> -hexane	bdl	1457	27	14	73	7370	bdl	27	bdl	13
2,3,4- <i>TM</i> -pentane	bdl	1271	16	11	17	688	bdl	17	bdl	26
Toluene	118	55,736	198	432	365	4275	156	864	176	168
2- <i>M</i> -heptane	bdl	801	bdl	bdl	22	2612	bdl	13	10	11
4- <i>M</i> -heptane	bdl	337	bdl	bdl	bdl	666	bdl	bdl	bdl	27
3- <i>M</i> -heptane	bdl	892	bdl	bdl	17	1664	bdl	13	bdl	34
Octane	bdl	591	bdl	10	54	5712	bdl	23	11	bdl
Ethylbenzene	27	3504	51	63	92	2676	37	122	35	49

Table 2 (continued)

Location	Pier A; 9 July 2004			Parking place; 9 July 2004			Pier B; 9 July 2004			IMK-IFU, Garmisch Rural site
	13:00	15:05	16:22	13:15	15:25	17:39	13:31	15:51	18:12	
Time	—	—	—	—	—	Re-fuelling of HB-IJS nearby	—	—	—	
Observations	—	—	—	—	—	—	—	—	—	
<i>m,p</i> -Xylene	104	12,167	126	214	235	4110	155	449	128	130
Styrene	117	182	157	76	63	960	199	162	199	197
<i>o</i> -Xylene	53	3199	56	80	121	2901	78	161	65	55
Nonane	15	102	15	18	67	5623	11	13	17	bdl
TVOC	4025	973,560	3232	7076	6014	73,972	3708	11,720	5674	7056
Benzene:Toluene	1.47	0.24	1.41	0.59	0.54	0.27	0.94	0.29	1.08	2.35

Listed are the samples in ambient air. bdl: below detection limit. “–999,999”: coelution. 999,999: no evaluation.

still relatively stable as characterised by the benzene:toluene ratio which is well below 1. At constant higher temperature, i.e. during taxiing, higher aromatics tend to crack leading to a less amount of these species, but increasing amounts of benzene. Thus for taxiing, a benzene:toluene ratio of about 1.6 is observed which is typical for kerosene exhaust (Spicer et al., 1985). In particular, during taxiing, high amounts of C₂–C₃ alkenes are observed. This status occurs after complete ignition, i.e. when the final temperature has not yet been reached, as it is the case under taxiing: this intermediate stage is characterised by high values of reactive alkenes as in the case of taxiing, but also enhanced values of high volatile alkanes and higher aromatics. The benzene:toluene ratio is similar to the ignition status. It should be noted also that isoprene is emitted in significant amounts. Isoprene is mostly emitted by biological sources, however over the last few years, it has also been found in traffic exhaust (Reimann et al., 2000; Borbon et al., 2001). Our study reveals that aircraft exhaust contains this highly reactive compound, in particular, during the taxiing and idle status of the engines.

4. Discussion

The measured concentrations of CO, NO_x, and VOCs characterise specific air quality levels at ground support locations of airports. The high correlation of CO concentration with aircraft movements is related to the typical emission characteristics of a jet engine. For idle power, jet engines emit high amounts of CO, due to incomplete combustion, and low amounts of NO_x, due to low

temperature. This is also reflected in the measured NO_x concentrations which show only little correlation with aircraft movements. High NO concentrations observed during the field experiment indicate young emissions of nearby sources. NO/NO₂ sources on the handling area are mainly ground handling vehicles which are usually powered by diesel or gasoline engines. The higher median concentration of NO/NO₂ on the “handling” path, which is mainly influenced by ground support emissions, highlights the importance of these kinds of emissions on airport air quality.

Emissions of aircraft at airports are usually calculated on the basis of certificated emission indices and traffic models for aircraft motions. The emission indices rely on well-defined measurement procedures and conditions during engine certification. Under real circumstances, however, these conditions may vary and deviations from the certificated emission indices may occur. The measured emissions indices are 0.4–2.2 times lower/higher than the certificated ones. Schäfer et al. (2003) also reported that real in use CO emissions are systematically higher than the ICAO test bed values, at least for some engines (e.g. the CFM56-5B category), while for others, the opposite is found. These variations are most likely caused by conditions under real circumstances which are different from the well defined conditions during the certification procedure. Nevertheless these differences are important since the ICAO data is currently used to calculate emissions from airports. In 2004, the A320 family (equipped with CFM56-5B engines) contributed at least 21.9% to all movements on the airport Zurich–Kloten (Unique, 2005).

Table 3
CO and VOC mixing ratios (in pptv, unless otherwise noted) in air samples taken in the exhaust plume of aircrafts

Engine status	12 July 2004; 12:35–12:44; HB-IPV				13 July 2004; 10:41–10:45; N69154				14 July 2004; 10:30–10:35; HB-IQH			
	Airport background	Ignition	Idle	Taxiing	Airport background	Ignition	Idle	Taxiing	Airport background	Idle	Taxiing	Taxiing
CO (ppbv)	84	140	794	3550	282	2165	2730	936	3139	3712	2090	196
Ethane	801	1198	1413	19,602	950	2986	3570	1314	6739	5278	2154	1362
Ethene	809	801	13,772	350,015	4343	49,028	53,250	5741	176,180	135,728	38,568	990
Ethine	193	353	4832	150,238	2052	24,672	27,693	2662	38,101	28147	9586	603
Propane	163	350	213	2327	150	3337	2811	406	4450	1500	730	944
Propene	213	164	3162	91,190	863	10,716	10,797	1005	42,327	28,393	6925	291
<i>i</i> -Butane	25	136	bdl	1339	bdl	35,913	274	121	35,810	161	149	185
Butane	105	438	107	2576	100	82,961	557	218	82,124	565	361	681
Propine + 1-butene	94	49	623	18,509	149	7466	1988	128	13,633	5664	1034	81
1,3-Butadiene	bdl	52	485	23,117	166	2480	2289	194	8671	4942	1196	29
<i>rr</i> -Butene	bdl	35	48	2322	22	13,291	240	28	13,834	480	75	bdl
<i>i</i> -Butene	41	40	269	7508	68	5448	903	125	7334	1000	380	44
<i>cis</i> -Butene	bdl	31	28	1450	bdl	8825	189	18	9370	406	95	14
3- <i>M</i> -1-butene	bdl	bdl	55	1620	bdl	1536	177	bdl	1940	456	112	bdl
1-Pentane	197	588	175	16,508	152	94,051	601	494	104,051	5041	5041	617
1-Pentene	46	14	311	6843	25	3637	703	36	6251	2599	505	bdl
2- <i>M</i> -1-butene	bdl	28	53	1975	bdl	6341	216	26	6835	343	153	25
Pentane	46	147	76	1572	51	22,446	302	211	22,139	626	196	245
Isoprene	24	31	91	3331	56	787	296	50	2829	644	367	36
<i>trans</i> -Pentene	bdl	21	37	1341	bdl	7521	269	13	7546	307	58	bdl
<i>cis</i> -Pentene	bdl	14	24	807	bdl	3852	80	bdl	3932	201	49	10
2- <i>M</i> -2-butene	bdl	25	18	715	bdl	10,368	84	17	9940	119	30	10
2,2- <i>DM</i> -butane	35	70	134	5944	76	11,929	437	101	11,771	835	271	102
<i>cyc</i> -Pentene	bdl	bdl	52	1199	bdl	798	114	12	1694	246	94	bdl
4 <i>M</i> +3 <i>M</i> -pentene	bdl	bdl	62	2008	bdl	500	190	bdl	1163	518	127	bdl
2,3- <i>DM</i> -butane	bdl	13	bdl	206	bdl	1938	32	16	2841	619	40	25
<i>cyc</i> -Pentane	bdl	37	bdl	411	bdl	8094	35	35	5682	167	40	46
2- <i>M</i> -pentane	41	116	41	985	58	22,164	152	113	19,940	185	165	206

The problems arising from the use of ICAO emission data in air quality investigations, due to its discrepancy to real in use conditions, has been recognized and the ICAO is working out new procedures to calculate aircraft emissions.

Typical ambient air VOC composition in the airport environment can be determined from the background samples taken during daytime at three different sites (Table 2). Basically, it is quite similar to urban background VOC split (EEA, 2001; Jorquera and Rappenglück, 2004). However, the airport background VOC composition also reflects the residual VOC mixture of aircraft and vehicle exhaust (ethene, ethine, propene) and fuel constituents (propane, butane, *i*-pentane). Benzene:toluene ratio shows a ratio of 1:3 which is representative for a mixture of traffic exhaust and kerosene evaporation.

VOCs at airports are released by aircraft exhaust, traffic exhaust, or fuel handling. VOC signatures could be clearly identified. Aircraft exhaust is largely dominated by high volatile and reactive C₂–C₃ alkenes. Also ethine can be found, a compound closely related to any VOC exhaust emission, including ground-based traffic. However this compound has a very low reactivity and is not critical in terms of local photochemical processes. Emissions from kerosene exhaust and refuelling can be discriminated by the benzene:toluene ratio since kerosene fuel tends to have an enhanced amount of higher aromatics. This also holds for ignition processes—contrary to taxiing—due to incomplete combustion. Kerosene refuelling also emits a large amount of unbranched alkanes. The study indicates that isoprene is formed in combustion processes of aircrafts.

It has to be stated that a discrimination between ignition and idle is difficult because the status of the engines were only determined subjectively, e.g. by feeling hot exhaust and observing noise changes.

Emission indices for hydrocarbons are given in the ICAO-database. To compare them with the presented VOC measurements, those samples with highest CO concentrations are assumed to represent taxiing aircraft. For these samples, the total VOC concentration reaches 780,608 pptv for the first aircraft (HB-IPV), while for the other two, the total amount is 3–7 times lower (117,037 pptv for N69154 and 243,771 pptv for HB-IQH). Hydrocarbon emission indices of ICAO for these three aircraft do not show such large differences (4.6 g kg⁻¹ for HP-IPV, 2.54 g kg⁻¹ for N69154 and 3.29 g kg⁻¹ for HB-

IQH), but a similar pattern is found when comparing measured CO emission indices of these three aircraft with ICAO. The determined real emission indices show large differences similar to VOC concentrations (70.7 g kg⁻¹ for HP-IPV, 16.9 g kg⁻¹ for N69154 and 28.6 g kg⁻¹ for HB-IQH), but the tabulated indices of the ICAO do not reflect these significant differences (44.8 g kg⁻¹ for HB-IPV, 19.23 g kg⁻¹ for N69154 and 23.51 g kg⁻¹ for HB-IQH). These findings indicate that CO and VOC have common aircraft emissions characteristics and hence, higher CO emissions (compared with ICAO) are also associated with higher hydrocarbon emissions. This is not unlikely as it can also be found in the ICAO database.

5. Conclusion

Results of air chemistry measurements with in-situ and open-path devices carried out at the airport Zurich–Kloten, Switzerland, during a field experiment from 30 June 2004 to 15 July 2004 have been presented together with data analysis for emission indices for CO and NO_x. CO concentrations in the vicinity of the terminals are dependent on aircraft motions and engine status, whereas NO_x concentrations are dominated by emissions from ground handling vehicles. This differentiation among the different emission sources has to be considered in air quality investigations. Especially for local air quality issues, aircraft emissions at airports are one important source of air pollutants, but ground support activities can't be neglected.

The comparison of calculated emission indices with those of ICAO shows higher real-world emissions than the ICAO-values for some engines, but slightly lower values for others. Overall, the real in use emission indices reveal differences of up to a factor of two compared to the certificated emission indices of ICAO, which are currently used to calculate aircraft emissions. The problems associated with the use of the certificated ICAO emission indices in emission calculations for air quality studies has been recognized and work to ameliorate emission calculation is already in progress by ICAO. Nevertheless, emission indices only partially describe the total aircraft emissions. Aircraft motion is another critical issue. To estimate overall uncertainties in emission calculations, further investigations are needed, comparable to those for vehicle emissions (Corsmeier et al., 2005).

VOC measurements within the airport environment are rare. Detailed results during ignition, idle and taxiing of aircrafts have been presented. The finding of previous test bed studies (Spicer et al., 1985) has been confirmed and highly reactive C₂–C₃ alkenes were found in significant amounts in the aircraft exhaust on an airport. The benzene:toluene ratio allows to discriminate refuelling emissions from exhaust emissions. The benzene to toluene ratio is well below 1 for refuelling emission and engine ignition while in the exhaust this value reaches up to 1.7. This indicates that, during ignition, the engine has not yet reached its final temperature and higher aromatic compounds are still relatively numerous. At constant higher temperature, i.e. during taxiing, higher aromatics tend to crack leading to less amount of these species, but increasing amounts of benzene. Our study revealed that though isoprene was not found in emissions from kerosene refuelling, it was detected in considerable amounts in the aircraft exhaust which indicates that isoprene is most likely formed in the combustion process of a jet engine.

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