Mapping air pollution in Taiyuan



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Summary

To demonstrate the usefulness of diffusive sampling in China, Taiyuan was chosen for mapping the ground level concentration of gaseous pollutants. Taiyuan, like several other cities is situated in a valley surrounded by mountains. Taiyuan has a stationary monitoring network of 13 stations with real-time instruments that measure pollutant concentrations at roof level. Air pollution levels of sulphur dioxide (SO2), nitrogen dioxide (NO2), ammonia (NH3), ozone (O3) and VOC (benzene, toluene, n-octane, ethyl benzene, m+p-xylene, o-xylene, butyl acetate and n-nonane) were here measured in Taiyuan in a joint project between IVL and CRAES (Chinese Research Academy of Environmental Sciences). Three weekly campaigns in August-September 2013 with 50 measuring sites were carried out. In a fourth campaign some measurements at industrial sites were carried out. The concentration maps show that SO2 and benzene concentrations are highest in the south-west part of Taiyuan while the NO2 concentrations are highest in the central parts. The ozone concentration is partly anti-correlated with NO2 and therefore has lowest concentrations in the central parts. The concentration of all pollutants increases from the first to the third campaigns.

Comparisons between concentrations at street level obtained with diffusive samplers and concentrations at roof level obtained with continuous instruments show reasonable results, except for ozone.

Introduction

Air pollution levels of sulphur dioxide (SO_2) , nitrogen dioxide (NO_2) , ammonia (NH_3) , ozone (O_3) and VOC (benzene, toluene, n-octane, ethyl benzene, m+p-xylene, o-xylene, butyl acetate and n-nonane) were measured in Taiyuan in a joint project between IVL and CRAES (Chinese Research Academy of Environmental Sciences). The main purpose of the study was to generate air pollution data with high spatial resolution in order to characterize the air quality situation in Taiyuan. An additional purpose of the campaigns was to introduce a cost-effective air pollution measurement technique, demonstrating its potential as an important support in air quality management for decision-makers.

The measurements were carried out using diffusive samplers and were organised in campaigns during three consecutive weeks in September 2013. Weekly samples were collected at 50 sites. The station network was designed by IVL together with staff from Taiyuan Research Institute of Environmental Sciences and CRAES. The siting of measurement stations was mainly classified as "urban background at street level". After sampling, all samplers were sent to IVL for analysis.

Short description of IVL's diffusive samplers

The samplers are developed at IVL in Gothenburg, Sweden. They were used for the first time in China in 1990. The sampler has a cylindrical shape, 25 mm in diameter and 12 mm thick. The gas enters the sampler through a membrane in the bottom. The sampling rate is determined by the diffusion coefficient for the gas and the dimensions of the sampler. Sampling starts as soon as the sampler is taken out from its box and stops when it is put back again. IVL's samplers contain stable chemicals that react with the gas forming a stable product. The average concentration of the gas during the exposure time is obtained with the diffusive samplers. Diffusive samplers have many advantages. They are small and silent and do not require electricity. They can therefore be placed almost anywhere. They can also be used for measuring background concentrations at very remote places and for a variety of different purposes. Four different IVL samplers were used in Taiyuan, SO₂, NO₂, NH₃ and O₃. A commercial sampler was also used to measure some traffic related VOC (benzene, toluene, noctane, ethyl benzene, m+p-xylene, o-xylene, butyl acetate and n-nonane). To be suitable for outdoor monitoring a special rain shield designed by IVL was used on the VOC sampler. All samplers are shown in Figure 1.



Aim of the project

The purpose of the study was to generate air pollution data with high spatial resolution in order to characterize the air quality situation in Taiyuan, and to demonstrate the usefulness of IVL's diffusive samplers. Here they were used for two different purposes; i) map concentrations at street level covering the whole city of Taiyuan, ii) a screening study outside some industrial plants.

Network of 50 stations

22 of the stations are classified as urban sites. One of those is close to a regular monitoring station. 28 sites are classified as city sites. 7 of those are close to regular monitoring stations. The city and the location of the sampling sites are shown in Figure 2. A site description is given in Table 1.

Additional sites

Diffusive samplers were also used for screening purpose at some industrial sites. A site description is given in Table 2.

Measurement campaigns in Taiyuan

There were four campaigns in total from August 30 to September 30. The first campaign took place between August 30 and September 5. At 3 sites all samplers were lost. The second campaign started when the first finished September 5 and went on until September 11. At the sites where samplers were lost in the first campaign, new samplers were not installed. In the second campaign all samplers at 2 more stations were lost. The third campaign took place 11 to 17 September. New samplers were then installed at the sites where the samplers were lost in the earlier campaigns. At three of the sites where samplers were lost in the first campaign and replaced in the third campaign, the samplers were not lost again. All samplers were, however lost at another site in campaign three where they had not been lost earlier. In this campaign samplers from 5 industrial sites were also taken. Start and stop dates varied from 11-13 September and 17-19 September respectively at the two industrial sites.

In the fourth campaign samplers were only installed at 3 of the original 50 sites. 7 other industrial sites were also used at this occasion. Sampling started between 17 and 19 September and ended between 23 and 25 September. After this two more samples were taken at the industrial sites.



Figure 2. Picture the locations of the 50 sites in Taiyuan.

Table 1. Site description with coordinates. u = urban, c = city, m = close to	a regular monit	oring site, L1 = lo	st
in 1 st campaign, L2 = lost in 2 nd campaign, L3 = lost in 3 rd campaign			

Site	Description	Lat	Latitude (N)		atitude (N)		Long	gitud	le (E)	height	info
		۰	ı	н	•	1	н	m			
A1	Kang Xi highway old toll station, Jian Caoping district	38	3	50.9	112	27	5.7	2.5	u		
A2	Bai Ban village, Jian Caoping district	38	1	36.7	112	28	27.6	5	u		
A3	Heavenly Kings temple, Zhaojiashan	38	1	50.8	112	33	39.7	2.5	u		
B1	North China University 1# teacher's apartment	38	0	37.4	112	26	23.5	2-3	u, L2		
B2	Xiang yang village	37	59	39.7	112	29	34.2	2.0	С		
B3	Taiyuan Gardens Bureau research center	37	59	27.8	112	31	20.6	2.5	С		
B4	China ordnance industries group Nearby Naizhai Park	37	58	50.8	112	32	0.2	3	c, m		
B5	Huanju village	37	59	45.8	112	37	7.1	2.5	u		
C1	Huyan village water factory	37	57	47.6	112	27	44.6	2	С		
C2	Chaixi Road XiZhangvillage Overspeed testing station	37	57	47.2	112	28	40.1	3	С		
C3	Xinhua hospital in Yingxin Street	37	57	36.8	112	31	35.4	4-4.5	С		
C4	Oil depot nearby Huanghouyuan	37	57	3.3	112	34	3.7	2	С		
C5	Xigang village committee	37	58	11.3	112	36	38.0	4	u		
D1	Jiancaoping District Environmental Protection Bureau	37	56	18.7	112	28	44.6	4	С		
D2	RuiCheng village	37	55	50.8	112	29	0.1	4	С		
D3	San du guan village	37	55	27.1	112	31	10.7	2.8	С		
D4	Bai yang shu transformer substation	37	55	27.5	112	34	0.0	5	С		
D5	Fu Le gerocomium in Zhangzitou village	37	55	30.9	112	36	50.5	3	u		
E1	Dayan village committee	37	53	27.0	112	26	43.9	2.5	u		
E2	the Love cashmere industry	37	53	19.2	112	28	37.1	2.5	С		
E3	Xinghua north street bilingual primary school	37	53	34.5	112	30	38.3	2.5	c, m		
E4	Jianhe river office	37	54	20.8	112	33	33.0	4	c, m		
E5	Wan shuntong training school for drivers	37	53	28.5	112	36	40.8	2	u		
F1	Nine Yard housing estate	37	51	20.4	112	26	14.9	2.5	u		
F2	Yingxi park	37	51	16.0	112	28	44.0	2.5	с		
F3	TERA	37	52	9.2	112	32	12.0	2.5	c, m		
F4	The JingXiu residential areas	37	51	12.2	112	34	4.9	2-3	С		
F5	SongZhuang High-speed intersection	37	51	13.4	112	36	46.5	3.0	u		
G1	Taoxing-housing estate	37	50	34.0	112	26	37.8	2.5	u		
G2	Huangpo village committee	37	48	58.3	112	28	43.9	4	c, L1		
G3	Wanguo- housing estate	37	48	59.3	112	31	30.9	2.7	с		
G4	Meikeyuan Urban Residential Areas	37	49	22.0	112	34	31.0	2.0	c, m		
G5	Nuodingshan Urban Residential Areas	37	48	54.0	112	37	1.0	2.2	u, L2		
H1	Mengshan Scenic Spots parking area	37	45	53.9	112	27	38.3	3.0	u		
H2	the kingdergarten first electricity residential areas	37	46	50.9	112	29	17.7	3.0	c, m		
H3	JinSheng middle school	37	47	3.6	112	31	2.4	2.5	c, L1		
H4	Longhaifangzhou Urban Residential Areas	37	47	2.0	112	33	54.0	2.2	c, L3		
H5	Shanxi safeguard employment training center	37	46	49.0	112	36	32.0	2.5	С		

Table 1. Continued

Site	Description	Latitude (N)		ude (N) Longitude (E)		height	info	
		0 I	н	0	۱.	н	m	
11	Tai mountain Scenic Spots parking area	37 44	49.4	112	26	7.6	3.0	u
12	GangLuan county town guchengying south	37 44	30.0	112	29	0.3	3.0	u
13	Shanxi sports center southwest corner	37 45	14.8	112	31	18.4	2.5	с
14	Nearby Jin energy thermal power plant	37 45	22.0	112	32	34.0	2.1	c, m
15	Foxconn East	37 44	49.0	112	36	12.0	2.3	u
J1	Jin temple park south gate	37 42	20.8	112	26	16.8	3.3	u
								u, m,
J2	JinYuan area government square	37 42	46.2	112	28	11.4	2.9	L1
J3	Beiwayao village south	37 42	31.1	112	31	12.6	3.5	u
J4	Jinshiyangguang water treatment Plant	37 43	1.5	112	34	11.4	2.2	С
J5	Tianzhuang village Urban Residential Areas	37 42	28.0	112	36	27.0	2.7	с
K1	kingdergarten in Dongpu village	37 40	33.9	112	31	20.3	2.8	u
K2	Primary school in Liujian village	37 40	44.4	112	33	34.9	2.5	u

Table 2. Site description with coordinates for the industrial sites.

Site	Description	Latitude (N)		Longitude (E)		e (E)	
		•	ı	н	•	ı	"
1	Nearby 2# boiler Taiyuan Iron and Steel(Group)Corporation	37	55	13.3	112	32	16.8
2	sintering machine tail in the third iron mill of Taiyuan iron and steel	37	54	40.1	112	32	54.4
3	Nearby coke oven in Qingxumeijin plant	37	35	18.7	112	18	39.9
4	Foxconn South	37	44	27.0	112	34	57.9
5	gas company gas station	37	53	44.6	112	32	30.0
6	ChenGuang vehicle gas filling station	37	53	24.9	112	32	13.4
7	Beside the painting workshop in Foxconn industrial park	37	44	48.8	112	34	43.9
8	Fu tung street east extension, at the entrance of construction sites	37	52	16.8	112	35	54.2

Results

The average concentrations during the four monitoring campaigns at the 50 sites are given in Tables 6 to 15. The variations between the 50 sites are small compared to other studies that we have performed (Cumbane et al., 2007; Byanju et al., 2012). The average concentration of all sites increases from the first campaign to the third. The rather few measurements in campaign 4 are very different from the first three measuring campaigns and seem strange.

Sulphur dioxide

The SO₂ concentrations are shown in Figure 3 and Table 4 in Appendix 1. The concentrations are rather high for being September, when heating homes have not yet started and radiation inversions does not make the situation worse . The coming new standard for annual mean concentration of SO₂ in China will probably be 60 μ g/m³ in cities. In many cases, the measured concentrations approach or exceed this value. The SO₂ concentration has a minimum in the north and a maximum in south-west.



Figure 3. SO₂ concentrations in μ g/m³ in the three campaigns (from the left).

Nitrogen dioxide

The NO₂ concentrations are shown in Figure 4 and Table 5. The NO₂ has a minimum in the north and a maximum in the centre of the map. The coming new standard for annual concentration of NO₂ in Chinese cities will probably be 40 μ g/m³, implying that the measured NO₂ concentrations are elevated. However, the concentrations have only been monitored for a rather short period. NO₂ is both a primary and secondary pollutant (from oxidation of NO) as will be seen in the ozone concentrations.



Figure 4. NO₂ concentrations in μ g/m³ in the three campaigns (from the left).

Ammonia

The NH_3 concentrations are shown in Figure 5 and Table 6. There are no obvious gradients for ammonia, but the sites E1 and F5 have higher concentrations than the other sites.



Figure 5. NH₃ concentrations in μ g/m³ in the three campaigns (from the left).

Ozone

There is a background concentration of O_3 coming from the stratosphere. The major part, however, comes from photochemical reactions in the near surface atmosphere. When ozone reacts with nitric oxide, nitrogen dioxide will be formed as a secondary pollutant ($O_3 + NO \rightarrow NO_2 + O_2$). The ozone concentration will thus be anti-correlated with secondary formed NO_2 . The anti-correlation between the ozone concentration and the total NO₂ concentration (primary emitted + secondary formed) is best seen in the second campaign, see Figure 6. The O_3 concentrations are shown in Table 7 and Figure 7. As can be seen in Figure 7, the ozone concentration is lowest in the centre of the map.







Figure 7. O_3 concentrations in μ g/m³ in the three campaigns (from the left).

Volatile Organic Compounds

Concentrations for the VOC are shown in Tables 8 – 15. At street level three of the measured VOC's i.e. benzene, toluene and the xylenes (orto-, meta- and para-) mainly originate from traffic. The concentration ratios toluene/benzene and (o-, m-, p-xylenes)/benzene are then rather constant from the traffic source. The toluene/benzene ratios seem to be around 1.7 in campaign three, but with a certain background concentration

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of benzene, see Figure 8. The xylenes/benzene ratios are similar, but with a somewhat higher number of outliers (non-traffic sources), see Figure 9. The three sites D5, J1 and H2 seem to have other sources than traffic for benzene as shown in Figure 8. These three and site H1 can also be seen below the straight line in Figure 9. Site K2 seems to have a non-traffic source for toluene or can be contaminated because it was not properly closed. K2 is, however, on the traffic line in Figure 9. The most obvious outlier for the xylenes is off the scale in Figure 9 (H5), see Table 13 and 14. Benzene is the most harmful compound for the human of the VOC components measured here. The European Union guideline for benzene as an annual mean is $5 \,\mu g/m^3$. The average concentration in campaign 3 is close to this value. The concentration distributions of benzene are shown in Figure 10.



Figure 8. Relationship between toluene and benzene concentration in campaign 3. The line is visually adapted to the points and has a slope of 1.7.



Figure 9. Relationship between the xylenes and benzene concentration in campaign 3. The line is visually adapted to the points and has a slope of 1.7.



Figure 10. Benzene concentrations in $\mu g/m^3$ in the three campaigns (from the left).

Ethyl benzene and n-octane are both correlated with benzene in a similar way as toluene and xylenes with a background concentration of benzene of 2 μ g/m³, indicating that they also mainly originate from traffic. The sites were all chosen here as far from traffic as possible. If some sites closer to traffic had been chosen, a better

VOC profile for traffic would have been obtained. Butyl acetate is not related to traffic and is sometimes used as solvent. The concentrations of butyl acetate were during the campaigns usually below the detection limit.

Comparison between concentrations at street and roof level

The results from measurements at street level with diffusive samplers were compared to results from the stationary monitoring network in Taiyuan. The stationary monitoring network consist of 13 stations equipped with continuous instruments that measuring concentrations of SO_2 , NO_2 and O_3 on an hourly basis at roof level (10.5 meters above ground). The coordinates for these stations and the site ID for the closest site with diffusive samplers at street level are given in Table 3.

Stationary monitoring station	Latituo	de (N)		Longitude (E)			Nearest
	o		п	0	1	п	site
Shang lan	38	0	38.8	112	26	2.5	B1
Nan zhai	37	59	7.3	112	32	58.0	A3,B4
Jian he	37	54	37.0	112	34	21.2	E4
Jian cao ping	37	53	14.3	112	31	18.3	D3,E3
Tao yuan	37	52	9.0	112	32	13.0	F3
Hao zhuang	37	51	35.0	112	35	35.0	(E5,F5)
Xi shan	37	51	11.0	112	27	17.0	G1
Cai yuan	37	50	33.0	112	33	45.0	F4
Chang fengxi	37	49	27.0	112	31	58.0	G3
Wu cheng	37	49	10.2	112	34	12.0	G4
Jin sheng	37	46	49.8	112	29	17.7	H2
Xiao dian	37	45	7.0	112	33	44.6	H4
Jin yuan	37	42	44.8	112	28	9.8	J2

Table 3. Stationary monitoring stations (Instruments) with coordinates and nearest street level site (diffusive samplers, see Table 1). Nearest sites within parenthesis indicate that the sites are far from the station.

The average SO_2 concentrations at the nearest stationary monitoring station during the same time interval as the diffusive samplers were measuring have been calculated (Table 16). The comparison when the data capture exceeded 90 % has been plotted in Figure 11. As expected the SO_2 concentrations are generally higher at roof level. One exception is the site Wanguo- housing estate (G3) which has a higher SO_2 concentration than the nearest monitoring site (Chang fengxi) during all three campaigns. It may have a SO_2 source nearby.

A similar plot for NO_2 is shown in Figure 12. Data are shown in Table 17. Since traffic is an important source for NO_2 , the concentrations should be higher at street level. This is also the case, which is shown in Figure 12.



Figure 11. Scatter plot of SO_2 concentration at roof level versus SO_2 concentrations at street level during the three measurement campaigns. The circled points belong to Chang fengxi and G3 (Wanguo-housing estate).



Figure 12. Scatter plot of NO_2 concentration at roof level versus NO_2 concentrations at street level during the three measurement campaigns.

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The results for ozone are shown in Figure 13 and data in Table 18. Since traffic emits large amounts of nitric oxide (NO) which "consumes" ozone, lower concentrations are expected at street level than at roof level. This is, however, not the case. The relation between the ozone concentration at street and roof levels seem to be site specific. The measured ozone concentration at some roof level stations are always higher than the O_3 concentration at the nearest street level site while some are always lower or always much lower than the nearest street level site. There is not much variation between the campaigns. The relationship between NO_2 and O_3 concentrations that are shown in Figure 6 is not obvious at the roof level stations.



Figure 13. Scatter plot of O_3 concentration at roof level against O_3 concentrations at street level during the three measurement campaigns.

Screening study at industrial sites

The results from measurements at the industrial sites are presented in Table 19 and 20 in the appendix.

Discussion

The measurement campaign in Taiyuan was carried out only during one month. Due to seasonal variations, mainly meteorological conditions, concentration levels of air pollutants will differ both within a year and between years.

From the results achieved so far it is however obvious that the use of diffusive samplers, in combination with a careful selection of measurement sites, is a useful strategy in mapping geographical variations in levels of air pollutants at ground level in Taiyuan, an area of complex emissions. Important support in air quality management has been generated during the short time period and at a reasonable cost.

From the concentration maps, one can see that SO_2 and benzene concentrations are highest in the south-west part of Taiyuan while the NO_2 concentrations are highest in the central parts. The ozone concentration is partly anti-correlated with NO_2 and therefore has lowest concentrations in the central parts. Ammonia shows a different pattern. The highest concentrations are found in the western and eastern parts. The concentration of all pollutants increases from the first to the third campaigns.

Comparisons between concentrations at street level obtained with diffusive samplers and concentrations at roof level obtained with continuous instruments show reasonable results, except for ozone.

By using air quality mapping at an early stage, monitoring programmes can be optimised so that siting of longterm monitoring stations will more adequately represent important areas e.g. with high source density or dense population. However, the results achieved regarding air pollution levels will not alone give information enough to be used as a basis for prioritization of the most relevant and cost-effective measures to reduce emissions and improve the air quality.

In areas with rapid urbanisation and a complex mixture of emissions the introduction of relevant and effective mitigation measures is highly dependent on the establishment of monitoring systems and emission databases coupled to dispersion models. A traditional build-up of an emission database requires lot of resources, both in terms of time and information needed. In order to promote early measures that counteract severe urban air pollution events, rapid risk assessment tools can be a useful tool.

IVL has developed a rapid emission inventory methodology, called the Rapid Urban Assessment (RUA) Concept that is relatively inexpensive and rapid to carry out, and still gives highly comparable results with more expensive bottom-up approaches. This method has been applied and tested in Sweden as well as in other parts of the world with good results.

The RUA concept is based on

- the rapid emission inventory method
- investigation of the use for this data in conjunction with simple dispersion models
- verification by mapping air pollution concentrations using low-cost monitoring technique

An emission database can be created using GIS; satellite pictures to define a land-use classification; identification of point sources; collection of information concerning major polluting sectors by diffusive samplers and, to a limited extent, more traditional emission inventory methods; use of the land-use data, weighted by population density to distribute the emissions etc. The emission database can then be linked to a suitable atmospheric dispersion model to develop modelled concentration estimates. These results will then be validated by comparison with the air pollution concentrations derived from mapping campaigns using diffusive samplers. The results can also be used to achieve exposure data which may be linked to doseresponse curves and economic assessment methods of impact for e.g. health, crops and material. The emission database can then be used as a basis for further improvement by using a bottom-up inventory approach and gradually replace rather rough estimates with more accurate activity data and emission factors for different industrial sectors as well as for the transport sector, add information on separate point sources, etc. IVL-report C 58 Mapping air pollution in Taiyuan

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Table 4. SO ₂ concentrations in	µg/m ³ at STP,	during the four	r campaigns.

site	1st	2nd	3rd	4th
A1	15	17	28	
A2	23	28	34	
A3	23	25	30	
B1	25			
B2	28	28	33	
B3	30	32	33	
B4	27	29	38	
B5	25	23	33	
C1	19	23	36	
C2	30	28	44	
C3	43	38	40	
C4	22	34	40	
C5	29	35	42	
01	20	20	74 /0	
D1 D2	52	50	45	
202	J4 40	27	10	
	40	27	40	
	30	38 27	43	
	33 25	37	48	
E1 E2	35	40	43	
EZ	50	58	55	
E3	47	51	58	
E4	44	46	50	
E5	37	45	45	
F1	53	51	52	
F2	63	61	69	
F3	38	39	50	
F4	43	41	47	
F5	31	38	48	
G1	52	49	51	
G2			52	<0.9
G3	58	55	54	
G4	42	41	47	
G5	42		39	
H1	65	54	33	
H2	58	48	65	
H3			49	<0.8
H4	54	56		
H5	43	42	46	
11	53	43	59	
12	54	56	70	
13	58	52	65	
14	47	47	53	
15	41	46	49	
J1	61	53	75	
J2			71	40
J3	45	38	54	
J4	43	45	57	
J5	41	40	50	
K1	41	40	58	
К2	38	37	52	
Average	41	41	49	

Table 5. N	10 ₂ concent	rations in µg	/m° at STP,	during the fo
site	1st	2nd	3rd	4th
A1	16	19	23	
A2	28	27	37	
A3	32	35	27	
B1	14			
B2	39	38	45	
B3	42	50	50	
B4	43	50	53	
B5	44	43	34	
C1	38	44	42	
C2	55	64	73	
C3	47	54	51	
C4	50	52	47	
C5	22	28	30	
D1	48	55	62	
D2	46	52	55	
D3	59	57	68	
D4	55	55	54	
D5	30	31	33	
E1	40	38	44	
E2	55	58	59	
E3	55	59	64	
E4	57	57	61	
F5	51	49	50	
F1	41	39	46	
F2	67	58	65	
F3	60	63	67	
F4	63	52	53	
F5	65 66	59	60	
G1	30	36	30	
62	39	50	50	24
62	62	57	50 64	24
64	64	57	04 E0	
G4 CF	64 60	59	50	
	40	11	20	
	49	41	51	
HZ	64	69	52	20
H3	C A	60	58	20
H4	64 50	60 5.0	- 4	
H5	56	50	54	
11	39	32	31	
12	62	58	61	
13	58	62	55	
14	59	64	64	
15	55	47	49	
11	46	39	38	
J2			56	56
13	42	44	35	
J4	47	48	50	
J5	45	41	43	
K1	51	52	51	
К2	42	36	41	
Average	48	49	50	

Table 5. NO₂ concentrations in $\mu g/m^3$ at STP, during the four campaigns.

Table 6. N	H ₃ concent	rations in µg	m at STP,	auring the to
site	1st	2nd	3rd	4th
A1	4	6	4	
A2	11	14	18	
A3	9	10	12	
B1	7			
B2	12	12	14	
B3	9	9	11	
B4	8	9	13	
B5	11	10	10	
C1	8	11	9	
C2	14	14	14	
C3	12	18	19	
	11	16	12	
C5	7	<u>а</u>	9	
	22	10	25	
02	10	19	23	
202	12	16	23	
	15	10	10	
	10	10	19	
	0	0	14	
E1 E2	37	28	38	
EZ	12	14	14	
E3	13	14	10	
E4	15	15	1/	
E5	11	8	12	
F1	9	11	17	
F2	1/	13	14	
F3	9	16	13	
F4	14	13	12	
F5	21	55	53	
G1	11	12	18	
G2			13	102
G3	13	12	16	
G4	12	11	13	
G5	13		18	
H1	10	9	16	
H2	13	14	17	
H3			22	95
H4	12	13		
H5	15	14	20	
11	11	7	17	
12	14	18	20	
13	15	21	20	
14	16	17	17	
15	11	14	18	
J1	12	14	18	
J2			14	11
J3	23	18	2	
J4	17	18	23	
J5	10	13	14	
К1	17	21	25	
К2	15	15	19	
Average	13	15	17	
	-	-	1	

		trationa in	3 -1 OTD		
Table 6.	INH ₃ concer	trations in µg/m	i at STP,	during the to	ur campaigns.

unocitaint	concentration.			
site	1st	2nd	3rd	4th
A1	63	69	81	
A2	61	65	76	
A3	44	48	77	
B1	66	_		
B2	39	54	61	
B3	35	37	54	
B4	35	37	54	
B5	37 //1	۶7 ۸7	72	
C1	25	47	82	
	20	45	75	
C2	29 40	41	75 64	
	40	40	04 70	
C4	42	49	70	
5	62	69	81	
D1	36	40	59	
D2	47	54	83	
D3	40	44	55	
D4	35	52	63	
D5	61	68	89	
E1	43	49	57	
E2	33	46	62	
E3	35	45	67	
E4	49	49	65	
E5	50	57	69	
F1	46	60	70	
F2	36	47	70	
F3	34	45	62	
F4	37	45	59	
F5	30	41	72	
G1	49	66	71	
G2			65	<5.4
G3	46	52	72	
G4	35	47	63	
G5	43		67	
H1	65	67	75	
H2	47	52	78	
H3			64	<5.2
H4	46	52		
H5	37	44	61	
11	54	65	95	
12	40	50	83	
13	48	51	78	
14	43	42	61	
15	44	54	71	
J1	60	68	94	
J2			78	41
J3	51	55	21	
J4	50	53	73	
J5	49	64	74	
К1	45	55	74	
К2	82	57	83	
Average	46	52	70	

Table 7. O_3 concentrations in μ g/m³ at STP, during the four campaigns. Red numbers denote damage samplers and uncertain concentration.

Table 8. Benzene concentrations in µg/m ³ at STP, during the four campaigns. Numbers in red indicate that t	he
plugs are poorly sealed and there is a high risk for contamination.	

site	1st	2nd	3rd	4th
A1	1.5	2.1	2.8	
A2	1.9	2.5	3.0	
A3		3.1	3.2	
B1	2.1			
B2	2.2	3.6	3.6	
B3	2.1	3.5	2.9	
B4	4.2	4.8	4.1	
B5	3.1	3.6	3.8	
C1	2.4	3.2	3.4	
C2	2.2	4.0	3.1	
C3	3.9	4.7	4.5	
C4	5.5	4.7	3.7	
C5	27	3.1	<i>J</i> .7	
CJ D1	2.7 / 1	4.0	4.1	
D1 D2	4.1 2 7	2.9	2.9	
D2	2.7	2.0	3.6	
03	20	3.8	3.0	
	3.8	4.0	4.4	
DJ E1	2.0	2.7	4.7	
E1 E2	3.1	4.0	3.7	
E2 E2	2.9	4.0	4.2	
	2.9	4.1	4.0	
E4	3.0	3.8	4.1	
E5	3.0	3.9	4.6	
F1 52	3.3	5.3	4.2	
FZ		4.3	4.5	
F3	2.2	4.2	4.3	
F4	3.2	4.1	4.4	
F5	3.8	4.3	6.0	
GI	3.5	4.4	5.1	
G2			5.5	8.8
G3	3.2	4.7	5.0	
G4		3.2	4.3	
G5	3.2	. .	5.3	
H1	3.9	6.5	6.7	
H2	5.1	6.2	7.3	
НЗ			4.1	8.8
H4	3.4	3.5	3.7	
H5	3.4	3.7	4.3	
11	3.7	4.2	5.2	
12	6.6	31	25	
13	3.8	6.1	4.2	
14	3.3	4.3	3.8	
15	2.9	2.6	3.5	
J1	5.3	6.2	5.8	<u> </u>
J2			21	31
13	3.5	4.1	6.3	
J4	2.8	3.2	3.4	
J5	2.9	2.8	3.3	
K1	3.6	3.3	4.4	
K2	2.9	2.8	3.6	
Average	3.3	4.6	5.1	

site	1st	2nd	3rd	4th
A1	1.5	0.8	1.0	
A2	1.9	1.4	1.9	
A3		1.8	1.5	
B1	2.1			
B2	2.2	2.1	3.3	
B3	2.1	3.1	2.3	
B4	4.2	3.0	4.4	
B5	7.2 2 1	3.0	1.4	
C1	2.4	2.4 2.1	2.2	
C1	2.4	2.4	2.5	
C2	2.2	20 E 0	2.2 1 E	
	5.9	5.2	4.5	
C4	5.1	3.9	3.5	
C5	2./	8.9	3.2	
D1	4.1	13	6.6	
D2	2.7	11	2.6	
D3		3.0	2.6	
D4	3.8	5.1	4.3	
D5	2.0	2.2	1.9	
E1	3.1	3.6	2.4	
E2	2.9	8.1	4.1	
E3	2.9	3.8	4.6	
E4	3.6	4.2	4.5	
E5	3.0	36	3.6	
F1	3.3	3.7	3.0	
F2		4.1	3.4	
F3		5.5	5.0	
F4	32	4 1	3.2	
F5	3.8	71	7.2	
G1	3.5	2.8	33	
G2	5.5	2.0	4.2	11
62	2 7	2 /	3.0	
	5.2	2.4	3.9	
04 CF	.	5.5	5.5	
	5.Z	2 4	5.1 7 r	
пт ⊔р	5.9 F 1	5.4 2.4	7.5	
	5.1	5.4	5.4	10
TI 3	2.4	FC	5.0	12
H4	3.4	5.6	2.9	
H5	3.4	9.7	5.9	
11	3.7	4.8	6.6	
12	6.6	5.8	4.8	
13	3.8	5.0	3.7	
14	3.3	7.2	4.3	
15	2.9	5.0	3.2	
J1	5.3	2.1	2.2	
J2			4.2	33
J3	3.5	2.7	7.6	
J4	2.8	3.6	2.8	
J5	2.9	3.2	2.7	
К1	3.6	2.5	5.2	
К2	2.9	4.2	8.0	
Average	3.3	5.7	3.9	
	0.0			

Table 9. Toluene concentrations in μ g/m³ at STP, during the four campaigns. Numbers in red indicate that the plugs are poorly sealed and there is a high risk for contamination.

poorly sea	poorly sealed and there is a high risk for contamination.								
site	1st	2nd	3rd	4th]				
A1	<0.15	<0.15	<0.15						
A2	0.3	0.3	0.3						
A3		<0.15	<0.15						
B1	<0.15								
B2	0.2	0.2	0.3						
B3	0.4	0.2	0.2						
B4	0.3	0.3	0.6						
B5	0.2	0.2	0.5						
C1	0.3	0.3	0.4						
C2	0.4	0.9	0.2						
C3	0.3	0.4	0.4						
C4	0.6	0.4	0.3						
C5	0.3	0.4	0.4						
D1	1.1	0.5	0.6						
D2	0.2	0.3	0.3						
D3		0.4	0.2						
D4	0.4	0.4	0.7						

0.2

<0.15

0.4

0.3

0.3

0.4

0.2

0.2

0.5

0.3

0.5

0.3

0.7

0.3

0.3

0.3

0.2

0.2

0.4

0.2

0.5

<0.15

0.3

0.2

0.3

0.2

0.2

< 0.15

0.3

0.2

0.3

0.3

<mark>0.3</mark> 0.3 1.7

1.8

0.6

D5

E1

E2

E3

E4

E5

F1

F2

F3

F4

F5

G1

G2

G3

G4

G5

Η1

H2

H3

Η4

Η5

11

12

13

14

15

J1

J2

J3

J4

J5

Κ1

К2

Average

< 0.15

0.3

0.3

0.2

0.4

0.3

0.2

0.2

0.4

0.4

0.3

0.3

<0.15

0.2

0.3

0.4

<0.15

0.2

<0.15

0.2

0.3

< 0.15

0.5

0.2

0.2

0.5

0.2

0.3

< 0.15

0.3

0.3

0.4

0.8

1.0

0.3

0.9

0.3

0.3

0.4

0.2

0.3

0.3

0.3

0.3

0.5

0.4

0.2

0.5

0.4

0.5

0.2

<0.15

0.3

0.3

0.2

0.2

<0.15

0.4

Table 10. n-Octane concentrations in $\mu g/m^3$ at STP, during the four campaigns. Numbers in red indicate that the plugs are poorly sealed and there is a high risk for contamination.

Table 11.	n-Butyl acetate	concentrations ir	n µg/m° at ST	P, during the four	r campaigns.	Numbers i	n red indicate	that the plugs
are poorly	sealed and ther	e is a risk for co	ntamination.					

site	1st 2nd		3rd 4th		
A1	<0.50	<0.50	<0.50		
A2	<0.50	<0.50	<0.50		
A3		<0.50	<0.50		
B1	<0.50				
B2	<0.50	<0.50	<0.50		
B3	<0.50	<0.50	<0.50		
B4	<0.50	<0.50	<0.50		
B5	<0.50	<0.50	<0.50		
C1	<0.50	0.1	<0.50		
C2	<0.50	<0.50	<0.50		
C3	<0.50	<0.50	<0.50		
C4	<0.50	<0.50	<0.50		
C5	<0.50	<0.50	<0.50		
D1	<0.50	<0.50	<0.50		
D2	<0.50	<0.50	<0.50		
D3		<0.50	<0.50		
D4	<0.50	<0.50	<0.50		
D5	<0.50	<0.50	<0.50		
E1	<0.50	<0.50	<0.50		
E2	<0.50	<0.50	<0.50		
E3	<0.50	<0.50	<0.50		
E4	<0.50	1.5	<0.50		
E5	<0.50	<0.50	<0.50		
F1	<0.50	<0.50	<0.50		
F2	<0.50	<0.50	<0.50		
F3		<0.50	<0.50		
F4	<0.50	<0.50	<0.50		
F5	<0.50	<0.50	<0.50		
G1	<0.50	<0.50	<0.50		
G2			<0.50	10.4	
G3	<0.50	<0.50	<0.50		
G4	<0.50	<0.50	<0.50		
G5	<0.50		37.6		
H1	<0.50	<0.50	0.8		
H2	<0.50	<0.50	1.1		
H3			<0.50	9.8	
H4	<0.50	0.5	<0.50		
H5	<0.50	<0.50	<0.50		
11	<0.50	<0.50	0.6		
12	<0.50	<0.50	0.8		
13	<0.50	<0.50	3.4		
14	<0.50	<0.50	<0.50		
15	<0.50	<0.50	<0.50		
J1	<0.50	<0.50	0.6		
J2			0.8	2.8	
J3	<0.50	<0.50	0.9		
J4	<0.50	<0.50	<0.50		
J5	<0.50	<0.50	<0.50		
K1	<0.50	<0.50	0.7		
К2	<0.50	<0.50	0.8		

plugs are p	oorly sealed a	and there is a	risk for contar	nination.
site	1st	2nd	3rd	4th
A1	0.2	0.2	0.3	
A2	0.3	0.4	0.7	
A3		0.5	0.5	
B1	0.3			
B2	0.7	0.6	0.8	
B3	0.8	1.1	0.8	
B4	1.0	1.0	1.1	
B5	0.5	0.7	0.5	
C1	1.0	0.6	0.9	
C2	0.8	1.1	0.7	
C3	1.4	1.2	1.2	
C4	1.5	1.4	1.0	
C5	0.7	0.6	0.7	
D1	4.4	1.0	1.3	
D2	0.9	13	0.9	
52	0.5	1.0	0.8	
D3	2.0	2.4	1 9	
	2.0	2.4	1.5	
DJ F1	0.5	0.5	0.5	
E1 52	0.9	0.8	0.6	
EZ	1.8	1.7	1.5	
E3	1.2	1.2	1.5	
E4	2.8	1.9	2.4	
E5	1.1	1.9	1.0	
F1	0.9	0.7	0.7	
F2		1.9	1.7	
F3		1.2	1.3	
F4	1.1	1.5	1.2	
F5	2.7	4.1	3.0	
G1	0.7	0.6	0.8	
G2			1.2	4.3
G3	1.6	1.6	1.9	
G4		1.7	1.1	
G5	1.4		44	
H1	0.6	0.8	0.8	
H2	1.2	1.2	1.1	
H3			2.4	4.3
H4	1.7	1.4	1.6	
H5	1.7	2.9	5.0	
11	0.4	0.4	0.5	
12	0.8	14	1.0	
12	1.6	3.1	2.2	
.σ ΙΔ	1.0	17	1 /	
15	1.4	0.7	1.4 0.0	
11	1. 4 0.7	0.7	0.5	
12	0.7	0.0	0.0	2.0
12	1.0	1 7	2.0	2.9
13	1.0	1.2	1.5	
J4	1.0	1.3	0.9	
J5	0.8	1.2	1.0	
K1	0.7	0.6	0.7	
К2	0.7	0.6	0.8	
Average	1.2	1.2	2.1	

Table 12. n-Ethyl benzene concentrations in $\mu g/m^3$ at STP, during the four campaigns. Numbers in red indicate that the plugs are poorly sealed and there is a risk for contamination.

site	1st	2nd	3rd	4th
A1	0.6	0.4	0.5	
A2	0.8	1.1	1.7	
A3		1.0	1.3	
B1	1.0	-	_	
B2	1.9	1.8	2.1	
B3	2.0	3.2	2.1	
B4	25	2.6	37	
B5	13	1 4	14	
C1	2.4	17	2.6	
C2	23	4.6	17	
C3	2.5	3.0	3.2	
C4	2.5 4 3	3.5	2.5	
C5	4.5 1 8	1.8	2.5	
	1.0	2.2	4.0	
D1 D2	7.0	2.5	2.5	
D2	2.5	3.2 2.5	2.5	
D3	2 7	2.5	2.0	
D4 DE	5.7	4.5	4.2	
	0.9	1.0	1.5	
E1	2.0	1.8	1.4	
EZ	3./	3.6	3.5	
E3	2.3	2.9	3.3	
E4	3.5	3.3	5.1	
E5	2.3	4.8	3.0	
F1	2.2	2.0	1.8	
F2		4.0	3.8	
F3		3.1	4.1	
F4	2.3	3.7	2.7	
F5	6.0	8.5	6.5	
G1	1.8	1.7	2.3	
G2			3.1	9.7
G3	3.3	3.3	4.0	
G4		4.0	2.5	
G5	2.7		79.7	
H1	1.2	1.9	1.7	
H2	2.3	2.6	2.3	
H3			8.1	10.2
H4	3.4	3.1	3.5	
H5	4.2	6.9	7.5	
11	0.9	1.1	1.1	
12	2.0	4	3	
13	3.8	7.6	5.1	
14	2.3	3.6	2.8	
15	3.0	1.6	2.0	
J1	1.4	1.3	1.2	
J2			2.8	6.5
J3	2.0	2.9	2.5	-
J4	2.2	3.2	2.2	
J5	1.9	2.8	2.4	
К1	1.9	1.4	1.7	
к2	1.6	1.1	17	
Average	2.5	2.9	4.4	
				1

Table 13. m. p-Xylene concentrations in $\mu g/m^3$ at STP, during the four campaigns. Numbers in red indicate that the plugs are poorly sealed and there is a high risk for contamination.

poorly seal	ed and there i	s a high risk f	or contaminat הייב	10N.
site	İst	2nd	3rd	4th
A1	<0.14	<0.14	<0.14	
A2	0.2	0.3	0.5	
A3		0.3	0.3	
B1	0.2			
B2	0.6	0.4	0.5	
B3	0.5	0.6	0.5	
B4	0.6	0.7	1.1	
B5	0.4	0.5	0.6	
C1	0.8	0.5	0.7	
C2	1.1	2.2	0.5	
C3	1.1	0.9	0.9	
C4	1.3	0.9	0.7	
C5	0.8	0.6	0.8	
D1	3.4	1.0	1.2	
D2	0.6	1.0	0.7	
D3		0.7	0.7	
D4	1.1	1.3	1.1	
D5	0.2	0.3	0.4	
E1	0.7	0.6	0.3	
E2	1.0	1.0	1.1	
E3	0.7	0.8	1.1	
F4	1.0	1.0	13	
F5	0.7	2.1	0.7	
F1	0.6	0.5	0.5	
F2	0.0	1.2	1.2	
F3		0.9	1.2	
F J	07	0.5	0.8	
F5	1.2	2.4	2.0	
C1	1.8	2.4	2.0	
62	0.0	0.5	1.0	2.1
62	1.0	1 1	1.0	5.1
G2	1.0	1.1	1.2	
04 CF	1.0	1.2	0.0	
65	1.0	0.0	20	
	0.4	0.6	0.5	
HZ	0.6	0.8	0.6	2.0
H3	0.0	0.0	2.1	3.0
H4	0.9	0.9	1.0	
H5	1.2	1.8	2.2	
11	0.2	0.3	0.3	
12	0.5	1.1	0.7	
13	1.1	2.4	1.5	
14	0.7	1.1	0.8	
15	0.9	0.5	0.6	
J1	0.4	0.4	0.3	
J2			0.9	2.2
13	0.6	0.8	0.7	
J4	0.6	0.8	0.6	
J5	0.7	0.9	0.9	
K1	0.6	0.4	0.4	
K2	0.4	0.3	0.7	
Average	0.8	0.9	1.4	

Table 14. o-Xylene concentrations in $\mu g/m^3$ at STP, during the four campaigns. Numbers in red indicate that the plugs are poorly sealed and there is a high risk for contamination.

Table 15. n-Nonane concentrations in µg/	m ³ at STP, during the four	campaigns. Numbers in red in	dicate that the plugs are
poorly sealed and there is a high risk for a	contamination.		

site	1st	2nd	3rd	4th
A1	<0.14	<0.14	<0.14	
A2	0.19	0.25	0.31	
A3		<0.14	<0.14	
B1	<0.14			
B2	0.30	0.17	0.30	
B3	0.15	0.25	0.15	
B4	0.26	0.35	0.34	
B5	0.28	0.19	0.46	
C1	0.20	0.15	0.40	
C2	0.40	0.47	0.33	
C2	0.40	0.37	0.33	
	0.23	0.32	0.55	
C4 C5	0.33	0.37 <0.14	0.20	
	0.42	<0.14	0.20	
	0.50	0.22	0.07	
	0.14	0.21	0.18	
D3	0.02	0.39	0.16	
D4	0.82	0.44	0.65	
D5	<0.14	<0.14	0.16	
E1	0.30	0.25	<0.14	
E2	0.32	0.43	0.35	
E3	0.21	0.35	0.32	
E4	0.52	0.30	0.40	
E5	0.22	0.40	0.30	
F1	0.17	0.29	<0.14	
F2		1.25	0.20	
F3		0.26	0.36	
F4	0.30	0.40	0.28	
F5	0.27	0.28	0.33	
G1	0.36	0.19	0.40	
G2			0.68	1.23
G3	0.42	0.36	0.41	
G4		0.32	0.26	
G5	0.21		0.36	
H1	<0.14	0.19	<0.14	
H2	0.16	0.24	0.16	
H3			0.51	1.16
H4	0.19	0.31	0.18	
H5	0.43	0.35	0.40	
11	<0.14	<0.14	<0.14	
12	0.18	0.29	0.18	
13	0.15	0.47	0.35	
14	0.17	0.35	0.24	
15	0.27	0.19	0.22	
J1	<0.14	<0.14	<0.14	
J2			<0.14	0.44
J3	0.24	0.32	0.24	
J4	0.16	0.25	0.15	
J5	0.19	0.22	0.27	
К1	0.52	<0.14	0.14	
К2	0.16	<0.14	0.17	
Average	0.30	0.33	0.31	

Table 16. SO_2 concentrations in μ g/m³ measured at roof level with continuous instruments and SO_2 concentrations measured with Diffusive samplers at the nearest street level site (see Table 3). Concentrations within parenthesis have less than 90 % data capture and are not included in the evaluation. The results are plotted in Figure 11.

Monitoring station	Dif	Diffusive sampler Instrument		Instrument		
	1st	2nd	3rd	1st	2nd	3rd
Shang lan	24.7			36.7		
Nan zhai	25.2	27.2	34.2	28.8	33.3	39.7
Jian he	44.3	46.3	50.2	49.7	55.0	56.4
Jian cao ping	43.6	44.3	48.7	41.0	45.0	48.7
Tao yuan	38.3	39.4	49.5	40.1	46.2	51.0
Hao zhuang	34.0	41.4	46.7	(51)	55.9	40.5
Xi shan	51.9	48.8	51.4	59.1	59.4	58.1
Cai yuan	43.4	41.4	46.6	(26)	(30)	(23)
Chang fengxi	57.8	55.1	54.3	34.8	38.0	37.9
Wu cheng	41.6	41.5	46.6	54.8	59.2	57.6
Jin sheng	57.6	48.1	64.6	69.2	69.8	68.0
Xiao dian	53.9	56.1		55.2	58.6	
Jin yuan			70.8			62.9

Table 17. NO₂ concentrations in $\mu g/m^3$ measured at roof level with continuous instruments and NO₂ concentrations measured with Diffusive samplers at the nearest street level site (see Table 3). Concentrations within parenthesis have less than 90 % data capture and are not included in the evaluation. The results are plotted in Figure 12.

Monitoring station	Dif	ffusive samp	ler	1	nstrument	
	1st	2nd	3rd	1st	2nd	3rd
Shang lan	13.9			16.3		
Nan zhai	37.4	42.1	40.1	25.5	29.0	27.5
Jian he	56.6	56.8	61.4	36.3	39.3	38.3
Jian cao ping	57.4	58.2	65.8	39.3	33.6	36.3
Tao yuan	60.4	62.5	66.5	32.8	32.8	34.7
Hao zhuang	58.4	54.1	55.4	(36)	33.7	30.1
Xi shan	39.2	36.3	39.2	36.8	33.4	37.4
Cai yuan	63.0	51.7	52.9	(263)	(47)	(47)
Chang fengxi	63.5	56.9	64.0	48.9	48.2	49.2
Wu cheng	64.1	59.4	58.2	69.9	63.8	56.8
Jin sheng	63.7	69.4	52.4	51.9	53.8	42.3
Xiao dian	64.2	59.7		37.3	37.4	
Jin yuan			55.6			40.5

Table 18. O_3 concentrations in μ g/m³ measured at roof level with continuous instruments and O_3 concentrations measured with Diffusive samplers at the nearest street level site (see Table 3). Concentrations within parenthesis have less than 90 % data capture. The results are plotted in Figure 13.

Monitoring station	Dif	fusive samp	ler		Instrument	
	1st	2nd	3rd	1st	2nd	3rd
Shang lan	66.2			67.2		
Nan zhai	40.2	42.7	65.3	47.4	50.4	70.8
Jian he	49.0	49.4	65.0	35.7	40.7	52.4
Jian cao ping	37.5	44.7	60.9	31.0	39.2	52.4
Tao yuan	34.5	44.7	62.5	31.4	34.7	47.1
Hao zhuang	40.0	49.1	70.2	(44)	46.3	60.0
Xi shan	49.3	66.0	71.5	30.6	35.7	39.2
Cai yuan	37.3	45.4	59.0	(38)	(52)	(43)
Chang fengxi	46.0	51.6	72.1	28.6	32.8	40.8
Wu cheng	34.9	46.9	62.6	46.9	51.1	63.7
Jin sheng	46.6	51.7	77.5	37.0	38.5	48.7
Xiao dian	46.2	51.5		41.1	43.4	
Jin yuan			77.7			52.6

Table 19. Concentrations of inorganic pollutants at the industrial sites in µg/m³. Red numbers denote damage samplers and uncertain concentration.

Site	Start	Stop	SO ₂	NO ₂	NH_3	O ₃
1	2013-09-12 10:45	2013-09-18 10:50	577	76	16	59
1	2013-09-18 10:50	2013-09-24 09:30	569	70	12	67
2	2013-09-12 11:40	2013-09-18 11:05	61	60	21	62
2	2013-09-18 11:05	2013-09-24 10:00	61	52	13	55
3	2013-09-13 09:30	2013-09-19 17:25	66	64	43	74
3	2013-09-19 17:25	2013-09-25 10:15	45	63	36	33
4	2013-09-17 10:20	2013-09-23 10:00	37	60	12	51
4	2013-09-23 10:10	2013-09-29 10:00	67	58	13	47
5	2013-09-18 09:23	2013-09-24 08:32	22	60	20	40
6	2013-09-11 14:25	2013-09-17 08:40	51	80	19	<5.4
6	2013-09-17 08:40	2013-09-23 08:50	29	77	19	40
7	2013-09-24 09:35	2013-09-30 09:55	84	67	15	45
8	2013-09-11 17:10	2013-09-17 14:15	46	63	19	64
8	2013-09-17 14:15	2013-09-23 16:15	23	56	24	43

1

Site	Start	Stop	Benzene	Toluene	n-Octane	n-Butyl acetate	Ethyl benzene	m, p-Xylene	o-Xylene	n-Nonane
1	2013-09-12 10:45	2013-09-18 10:50	3.7	2.3	0.24	0.77	1.1	2.6	0.65	0.26
1	2013-09-18 10:50	2013-09-24 09:30	4.5	3.6	0.51	0.56	1.1	2.6	0.66	0.37
2	2013-09-12 11:40	2013-09-18 11:05	20	6.0	0.24	1.2	2.9	6.3	1.7	0.30
2	2013-09-18 11:05	2013-09-24 10:00	10	20	0.27	1.0	2.5	4.7	1.3	0.19
3	2013-09-13 09:30	2013-09-19 17:25	10	3.2	0.29	<0.50	0.67	1.5	0.36	0.43
3	2013-09-19 17:25	2013-09-25 10:15	25	4.9	0.51	0.62	0.83	2.8	0.71	0.49
4	2013-09-17 10:20	2013-09-23 10:20	3.3	2.2	<0.15	<0.50	0.82	1.7	0.45	<0.14
4	2013-09-23 10:10	2013-09-29 10:10	6.9	7.3	0.65	6.7	2.4	6.1	2.1	0.57
5	2013-09-18 09:23	2013-09-24 08:32	7.7	13	1.4	1.5	3.2	8.2	2.4	0.71
6	2013-09-11 14:25	2013-09-17 08:40	5.4	8.0	0.81	1.6	2.0	5.7	1.7	0.70
6	2013-09-17 08:40	2013-09-23 08:50	15	84	9.4	4.3	14	60	16	3.5
7	2013-09-24 09:35	2013-09-30 09:55	6.4	41	0.59	41	8.2	16	6.4	0.55
8	2013-09-11 11:10	2013-09-17 14:15	4.4	3.6	0.19	0.79	0.99	2.3	0.65	0.20
8	2013-09-17 14:15	2013-09-23 16:25	5.1	4.5	0.40	0.82	1.4	3.4	0.90	0.36

Table 20. VOC concentrations in μ g/m³ at STP at the industrial sites. Numbers in red indicate that the plugs are poorly sealed and there is a high risk for contamination.

Appendix 2 Additional information on IVL's Diffusive samplers

Principle behind diffusive sampling

Diffusive sampling is a passive technique. The samplers are therefore often called passive samplers. Passive sampling implies that no energy in the form of fuel or electricity has to be used. The energy comes from the kinetic energy of the gas molecules (the Brownian motion), which is a function of the air temperature. There are many types of passive samplers such as precipitation collectors and surrogate surfaces for particulate matter. The word diffusive sampler is specific for these samplers and will therefore be used here instead of passive samplers. The technique has been known since Palmes and Gunnison published the first work in 1973. Some years later they made a new design (Palmes and Gunnison 1976) which was applicable fore sampling of both SO₂ and NO₂. This sampler was designed for indoor use (no wind) and high concentrations. It consisted of a long tube open in one end and containing an impregnated screen in the other end. If the impregnation absorbs the pollutants rapidly, the concentration will be zero in the closed end. The open end will have the same pollutant concentration as the surrounding air. If the concentration in the surrounding air is constant, the pollutant concentration will decrease linearly with the distance in the tube. This decrease (concentration difference divided by the length of the tube) is called a concentration gradient. There is a simple relationship between the concentration gradient, the trapped amount of the gas to be measured, the diameter of the tube, the exposure time and the diffusion coefficient for the gas (Fick's first law of diffusion). If the impregnated filter has trapped all molecules of the targeted pollutant that has hit the filter and the concentration in the air has been constant, the average pollutant concentration can be calculated from the analysis of the impregnation and average air temperature. Pollutant concentrations are, however, not constant in the air. There was a myth in diffusive sampling that the samplers were not giving the correct average concentration if the pollutant concentration varied during sampling. It can be shown mathematically that the correct average concentration is obtained even if the pollutant concentration fluctuates. A more detailed description of the theory behind diffusive sampling has been made (Ferm, 2001a).

Often an experimentally determined uptake rate is used instead of Fick's law of diffusion. If Fick's law does not give the correct concentration, something is wrong. There may be a problem with the analysis, the trapping agent is not a perfect sink or the air molecules are not only transported by molecular diffusion.

Description of IVL's diffusive samplers

IVL has developed a diffusive sampler that follows Fick's law of diffusion. It can also be used outdoors and also for very low concentrations at places far from pollutant sources. This sampler has been used in China since 1990 (Ferm and Rodhe, 1997; Carmichael et al., 1995; Carmichael et al., 2003; Mi et al., 2006; Zhao et al., 2008).

Much effort has been used in finding chemical reactions that can trap the pollutants in a stoichiometric way. Inorganic compounds have been chosen instead of organic ones for impregnation of filters. Inorganic compounds are usually more stable than organic compounds. In this way the samplers can be stored at room temperature before as well as after sampling has been made. Sampling can in this way be performed at places far from the laboratory and at places lacking refrigerator. Forest research sites normally lack electricity and surface ozone is a regional problem that threatens people's health and makes large damages to crops. The areal distribution of surface ozone over Sweden is shown in figure 14. As can be seen from the figure, the urban concentrations are not much lower than the regional concentrations.



Figure 14. Ozone concentrations measured with IVL's diffusive samplers. Measurements were made March 2013 at background sites in Sweden. The location of Gårdsjön (Fig 15) is indicated with a red star.

Preparation and analysis of IVL diffusive samplers

Unlike instrumental measurement techniques, IVL's diffusive samplers does not need gas phase calibration. The sampler is disassembled in the laboratory and the impregnated filter is leached in a known amount of water with or without ionic medium. The liquid is analysed using an ion chromatograph or a spectrophotometer. These instruments have, however, to be calibrated. At IVL commercial certified standards are used to calibrate the instruments. Stable reference solutions are purchased from another company and used to check that the instruments always give the same response. By using specially trained personnel for the analysis and well documented procedures, diffusive samplers can for instance be used to study the concentration trends over time. The procedure for preparing and analysing the samplers has not changed since the start. A change in analytical procedures can be a large problem when long trend studies are made.

Figure 15 is an example of a 20 year long trend in surface concentration of ozone at a remote forest site in Sweden. The seasonal trend with spring maxima in ozone concentration is obvious.



Figure 15. Monthly surface (3 m above ground) ozone concentration measured with IVL diffusive sampler at the forest site Gårdsjön. Annular (Jan-Dec) average concentrations are shown as red squares.

The concentrations obtained with diffusive samplers are also continuously compared to active sampling at some sites in Sweden. This comparison has been going on for many years. When two techniques are compared and not agree, one has to look for errors in both techniques. Such comparisons have also been made occasionally to check other measurements not operated by IVL. Errors such as numbers reported in the wrong unit have been discovered in this way.

Figure 16 shows a comparison between UV instruments and diffusive samplers at three sites (Sjöberg et al., 2001).

Comparisons between instruments and diffusive samplers have also been made in a wind tunnel at varying wind speeds, temperatures and humidity (Ferm 2001b).



Figure 16. Comparison between diffusive (monthly means) and real-time measurement of ozone at three Swedish background stations during 2000.

Measuring ranges of IVL's diffusive samplers

The lower and upper detection limits depend on the blank and capacity of the impregnated filter. The corresponding concentration in the air therefore depends on the exposure time. The lower detection limit is based on three times the variation in the blank of an unexposed filter. The upper limit is based on the stoichiometric amount on the filter for the reaction with the pollutant in question and a safety factor. The normal sampling time for diffusive sampling in ambient air is one month. In Figure 16, the approximate measuring ranges for one-month sampling are given. The concentration limits are inversely proportional to the exposure time. If you want to calculate it for a shorter time interval, the numbers below should be multiplied by one month and divided with the exposure time in question. For sampling times exceeding one month, a sampling time of one month is used for calculation of the concentration.

Example

The measuring range for sulphur dioxide during 40 hours is:

Lower det.limit =
$$\frac{24 \cdot 30 \cdot 0.1}{40} \approx 2 \,\mu \text{g m}^{-3}$$

Upperdet.limit = $\frac{24 \cdot 30 \cdot 100}{40} = 1800 \,\mu \text{g m}^{-3}$

Volatile Organic Compounds (VOC) can also be measured using diffusive sampling. The exposure time should, however, not exceed one week (Tenax) and the temperature should not exceed 25 °C. Another sorbent (Carbopack B) can be used up to 2 weeks and at higher temperatures. At ambient temperatures around 25 °C it can even be used up to one month.

	-3
gas nitro con dioxido. NO	μg Π
nitrogen dioxide, NO_2	0.1-100
ozone, O ₃	1-100
ammonia, NH ₃	0.2-30
nitric acid, HNO ₃	0.03-10
sulphur dioxide, SO ₂	0.1-100
formic acid, HCOOH	1.5-150
acetic acid, CH ₃ COOH	1.5-250
hydrogen fluoride, HF	0.2-70
hydrogen chloride, HCl	0.5-100
mercury, Hg ⁰	0.001-
formaldehyd, HCHO	0.03-210
H_2S	0.5-5
benzene	0.32-37
toluene	0.23-23
n-octane	0.04-60
ethyl benzene	0.015-58
m+p-xylene	0.058-60
o-xylene	0.015-68
n-nonane	0.075-55

Figure 16. Measuring ranges for some pollutants calculated for one month exposure time.

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