Partitioning of formaldehyde between gas phase and particles (PM$_{2.5}$) in México City

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RESUMEN

Se utilizó una técnica de muestreo con despojadores anulares/filtros para determinar la partición fase gas-partícula de formaldehído en PM$_{2.5}$ en la Ciudad de México durante periodos cortos de tiempo. El formaldehído se colectó usando derivados de DNPH y analizándolos por HPLC/UV. Se usó un primer despojador para atrapar el formaldehído en fase gas, seguido de un filtro de Teflón para colectar las PM$_{2.5}$, un segundo despojador fue usado para atrapar el formaldehído desgasificado de las partículas colectadas en el filtro. Justo una vez finalizado el muestreo los filtros fueron almacenados en una solución de DNPH para fijar el formaldehído contenido en el filtro, y los despojadores fueron extraídos con otra solución de DNPH. La suma de las concentraciones en ambas fases va de 7.90 a 44.60 µg/m^3 durante los periodos de tiempos de 8 a.m. a mediodía en varias ocasiones del 2000 al 2003. En promedio, el cociente de formaldehído PM$_{2.5}$/fase gas fue de 0.15, cien veces más alto de lo previamente observado. Una gran fracción del formaldehído en partículas puede facilmente perderse por la combinación de tres procesos: dos de los cuales son la de gasificación por arrastre de aire y el desplazamiento del equilibrio entre fases, ambos bien conocidos y confirmados en otros estudios y un nuevo tercer proceso llamado extrusión, que también fue confirmado por experimentación. Aunado a esto, las PM$_{2.5}$ pueden actuar como un almacenamiento temporal o una fuente lenta de desprendimiento de formaldehído en el esmog fotoquímico de la Ciudad de México.

ABSTRACT

An annular denuder/filter-pack sampling technique has been employed to get an insight of the formaldehyde partitioning between gas phase and particles (PM$_{2.5}$) in México City using short time sampling periods. Formaldehyde was trapped using DNPH derivatives and analyzed by HPLC/UV. One annular denuder was used to trap formaldehyde from the gas phase followed by a Teflon filter to trap PM$_{2.5}$, and a second backup denuder was used to trap degassed formaldehyde from the filter. Just after finishing the sampling, filters were soaked in a DNPH solution to fix the PM$_{2.5}$ formaldehyde, and the denuders where extracted with another DNPH solution. The sum of the concentrations in both phases ranged from 7.90 to 44.60 µg/m^3 during the

sampling periods from 8 a.m. to noon in several ocassions from 2000 to 2003. In average, the formaldehyde $PM_{2.5}$/gas-phase ratio was about 0.15, one hundred times higher than previously observed. A large fraction of the formaldehyde in particles is easily lost by a combination of three processes: two of these, blow off from the trapped particles and displacement of the phase equilibrium, both well known and confirmed in other studies. A third process called extrussion of particles is described. Thus, $PM_{2.5}$ may act as a temporal sink or a slow releasing source of formaldehyde in México City's photochemical smog. This findings may have strong implications for air quality modeling.

1. Introduction

Carbonyl compounds are common trace components in the atmosphere, in particular in polluted urban environments (Grosjean, 1982). They play an important role in several atmospheric processes. Carbonyl compounds are common primary pollutants, mainly as residues from incomplete combustion processes (Kawamura *et al*., 2000). Moreover, carbonyls are also secondary pollutants which inevitably act as intermediates in the photo-oxidation of other volatile organic compounds in the atmosphere (Finlayson-Pitts and Pitts Jr., 1986). They are easily photolyzed, in particular formaldehyde and acetaldehyde, and can be the main free radical source in polluted atmospheres (Carlier *et al*., 1986). Carbonyl compounds, and in particular aldehydes, are known as toxic compounds (causing eye and lung irritation); and both formaldehyde and acrolein are suspected to be carcinogenic agents (Suh *et al*., 2000). Furthermore, some secondary compounds formed by degradation reactions of aldehydes such as peroxyacylnitrates, are much more hazardous (Stupfel, 1976).

Most of our knowledge about formaldehyde in the atmosphere comes from gas phase measurements. Formaldehyde is present in urban air at concentrations ranging from 2 to 156 ppb (2.45 to 191.41 µg/m³) (Grosjean, 1982; Grosjean *et al*., 1990; 1992; Báez *et al*., 1995; Possanzini *et al*., 1996). Like in rain and fog (Klippel and Warneck, 1978), carbonyl compounds could easily interact with particles as a result of their polar nature. Thus, a complete description of the aldehyde budget in the atmosphere requires cuantification of the concentration of aldehydes in both the gas phase and in the particles.

Very few reports have examined formaldehyde in particles. Concentrations found in polluted cities from developed countries such as Los Angeles, during the late seventies and early eighties ranged from 0 to 264 ng/m³ (Grosjean, 1982). In developing countries, up to 27.32 ng/m³ of formaldehyde were reported in particles in Brazil (Andrade and Pinheiro, 1993). Formaldehyde is a very volatile compound, with a molecular weight of 30 atomic mass units. Accordingly, it has been assumed that such a light VOC should not be present in the suspended particles as part of photochemical smog (Grosjean and Seinfeld, 1989). Other reports of formaldehyde in suspended particles (Klippel and Warneck, 1980) have been criticized on these grounds (Dasgupta, 1981). Furthermore, most of the reported studies of formaldehyde in particles were carried out using high volume samplers and long sampling periods.

Historically, air pollution standards for air quality compliance regarding suspended particles have been weight-based and time-averaged. Generally, the standard protocols for sampling are based on

high volume sampling for long times (i.e., 24 hours). These techniques were used to study the chemical composition of suspended particles. As discussed by Chow (1995), sampling artifacts produced by these methods are well documented for semi-volatile organic compounds (see the revised TO-13A method (CERI, 1999) and references 12-21 therein). One artifact is sample blow off and another equilibrium-shift. Equilibrium shift refers to the displacement of the partitioning equilibrium between the two phases when the compound of interest follows a daily pattern, such as formaldehyde does. Formaldehyde-rich particles trapped during the hours of high aldehyde concentrations will loose it when they get in contact with sampled air with lower concentrations some hours later. Most likely, all light VOC such as formaldehyde, if present in suspended particles trapped using high volume samplers, will be depleted from the filters by both processes during sampling. In addition, filters are commonly stabilized and weighed following standard protocols to obtain TSP, PM_{10} or $PM_{2.5}$ mass before being subjected to chemical analysis. The equilibrium-shift artifact is still at work while the filters are stabilized in the clean environments required by these protocols. For this reason, light VOC in suspended particles need to be extracted from the filters as soon as the sampling is performed. In addition, the use of short sampling times and low sampling flows are required to reduce looses by blow off and equilibrium-shift.

For semi-volatile compounds as PAH (CERI, 1999), blow off and equilibrium-shift sampling artifacts have been addressed by use of backup traps such as polyurethane foams or XAD2 resins down-stream in the filter. However, using this method no insight on the partitioning of the compound between the gas and the solid or liquid phase can be obtained. The concentration of the compound found in the backup trap will be the sum of the remaining gas phase content and the amount lost from the filter due to blow off and/or equilibrium-shift.

The present contribution describes an annular denuders set up designed to analize formaldehyde in both the gas phase and in suspended particles. We describe experiments supporting our findings that relatively high concentrations of formaldehyde are weakly bound to fine suspended particles.

2. Experimental procedures

Gas phase formaldehyde was sampled using the well know annular denuders technique (Grosjean et al., 1990). Figure la shows the sampling set up. This allows distinguishing between formaldehyde in the gas and particulate phase. This design has been tested for other semi volatile organic compounds (Coutant et al., 1992; Gundel et al., 1995). Samples were taken at a flow rate of 10 L/min. The annular denuders (URG, Chapel Hill, NC) are made of three concentric glass tubes with a 1 mm gap between them. These denuders were impregnated with 5 mL of dinitrophenylhydrazine (DNPH) solution prepared as described below. $PM_{2.5}$ particles were collected on Teflon filters of 47 mm in diameter and a pore size of 0.45 mm (Gelman Science, Ann Harbor MI) held in a filter pack (URG). A cyclone adapter (URG) was used to eliminate particles greater than 2.5 mm. Another denuder, 150 mm long was impregnated with 10 ml of 10% KI solution to scavenge ozone thus avoiding the artifact produced by it (Williams and Grosjean, 1990). After impregnation with the corresponding solution, the denuders were dried with a nitrogen flow at 2 L/min, closed with their caps and sealed with Teflon film to prevent contamination.

The DNPH solution used to recover the denuder's walls was prepared by adding 1% of recrystallized DNPH (chromatographic grade, Sigma-Aldrich, St. Louis, MO) in 1.5% H_3PO_4-acetonitrile (chromatographic grade, Merck, Hohenbrunn, Germany) solution by volume. The 10% KI-water solution used to recover the 150 mm denuder's walls was made with analytical grade KI (Merck).

As soon as each sample was collected, the Teflon filters were placed in a polyethylene bottle (Nalgene, Rochester, NY) and reacted with 20 ml of a 0.1% DNPH solution for 20 min, under sonication. The formaldehyde derivatives in the denuders were extracted with two 10 ml aliquots of acetonitrile and mixed together. On doing so, we were able to ''freeze'' the very volatile formaldehyde in particles, but lost the capability to measure the mass of trapped particles.

Field blanks were prepared for the DNPH coated denuders and for the Teflon filter at the beginning and at the end of the sampling campaign. The sampling train was mounted as described above and retrieved after at least 30 min. The denuders and filters were handled following normal procedures. In the D_i^1 and D_i^2 denuders (Fig. 1), the DNPH-CH_2O contamination was equivalent to a 4-hour average concentration of 6 ng/m^3 in air. In the Teflon filter extract, the DNPH-CH_2O contamination was equivalent to 30 ng/m^3.
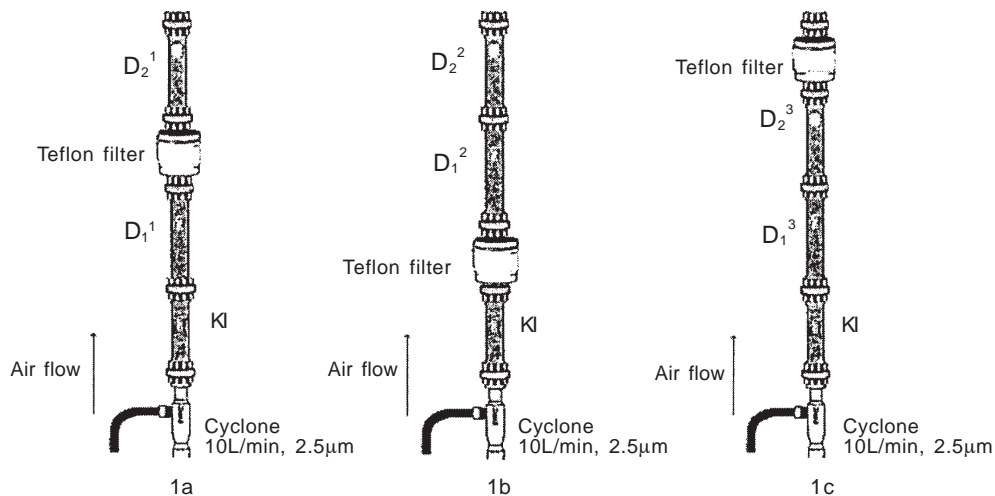

Fig. 1. Set up 1a, 1b, 1c.

Standard solutions of formaldehyde used for calibration were made by precipitation of standard solutions (Merck) using DNPH recrystallized twice following a known method (Shriner *et al.*, 1964).

Analyses were done by HPLC with an LC1150 HPLC pump (GBC) equipped with a 20 μL injector loop. A Shperisorb 5S 150 mm × 46 mm i.d. column was used for separating the compound matrix. For detection, a UV/VIS detector (Perkin Elmer, LC 1200) at 350 nm was used. An acetonitrile: water mixture (55:45 in volume) with a flow rate of 1.0 mL/min served as mobile phase.

3. Results and discussion

Before performing the experiments described in this paper, we carried out sampling of CH_2O in gas phase using the annular denuders system as reported by Possanzini *et al.* (1987). Just by curiosity we added a DNPH-coated Nylon filter after the single DNPH-coated denuder. High concentrations of formaldehyde were observed in the Nylon filter. Although these data will not be shown here, they posed several questions: (1) How much of that formaldehyde was due to contamination of the Nylon filter? (2) How much was due to a poor sampling efficiency of the denuder? (3) How much of it could be formed on site by oxidation of some precursor in the trapped particles? (4) How much was actually in the trapped particles before sampling?

To have better control of our experiments and before addressing the four questions we modified the sampling set up to the configuration shown in Figure 1a, replacing the DNPH-coated Nylon filter by a more inert Teflon filter and a second DNPH coated denuder. Such configuration is based on the following assumptions: All formaldehyde found in D_1^1 should be gas-phase formaldehyde. That found in T1, should be particle-bound. Formaldehyde trapped in D_2^1 should be weakly bound to T_1, lost to the formaldehyde-free airflow due to the blow off and equilibrium-shift artifacts. This set up follows other designs to trap inorganic acidic and basic compounds (Coutant *et al.*, 1992; Gundel *et al.*, 1995).

For all experiments described in this paper, samples were taken on the roof of the Center for Atmospheric Sciences in University Campus at the south of México City. They were always taken from 8 to 12 am. Filters were immediately transferred to the 0.1% DNPH solution in acetonitrile and sonicated. Denuders were always extracted just after the end of the sampling period.

Table 1 shows a much higher concentration of atmospheric formaldehyde in particles than previously reported and accepted. Klippel and Warneck (1980) reported 10^{-4}-10^{-3} particle/gas ratio. Even these values were criticized on the grounds of equilibrium considerations (Dasgupta, 1981). We have found much higher ratios, from 0.1 to 0.17 particle/gas ratio.

Table 1. Concentrations of atmospheric formaldehyde in gas phase (D^1), Teflon filters (F) and backup denuder (D_2), phase distribution ratio and some relevant environment properties.

Date	T °C	RH %	D_1 µg/m³	F µg/m³	D_2 µg/m³	F+D_2 µg/m³	D_1+F+D_2 µg/m³	(F+D_2)/D_1	PM_{10} µg/m³
11-30-01	14.4	46	14.83	0.25	2.58	2.83	17.66	0.19	50
12-03-01	12.0	63	8.56	0.29	1.45	1.74	10.30	0.20	46
12-05-01	10.8	68	8.13	0.15	1.37	1.52	9.65	0.19	48
12-07-01	11.0	63	21.26	0.31	3.17	3.48	24.74	0.16	103
12-10-01	12.2	53	11.39	0.25	1.72	1.97	13.36	0.17	62
12-11-01	12.8	78	6.82	0.12	1.02	1.14	7.96	0.17	38
			11.83	0.23	1.89	2.11	13.94	0.18	38

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Table 1. Concentrations of atmospheric formaldehyde in gas phase (D_1), Teflon filters (F) and backup denuder (D_2), phase distribution ratio and some relevant environment properties.

Date	T °C	RH %	D_1 µg/m³	F µg/m³	D_2 µg/m³	$F+D_2$ µg/m³	D_1+F+D_2 µg/m³	$(F+D_2)/D_1$	PM_{10} µg/m³
07-12-02	14.0	93.4	8.32	0.16	0.67	0.83	9.15	0.10	22
07-13-02	16.4	86	5.94	0.56	0.32	0.88	6.82	0.15	11
07-14-02	15.5	ND	7.27	0.84	0.60	1.44	8.71	0.20	20
07-15-02	16.6	ND	10.43	0.27	0.40	0.66	11.09	0.06	22
07-16-02	15.1	ND	11.16	0.17	0.48	0.65	11.81	0.06	24
07-17-02	16.1	ND	10.73	0.15	0.56	0.71	11.44	0.07	15
			8.98	0.36	0.50	0.86	9.84	0.11	
01-23-03	10.6	66	36.09	0.54	1.94	2.48	38.57	0.07	37
01-24-03	10.2	50	22.13	0.41	2.28	2.69	24.82	0.12	61
01-25-03	12.8	66	19.65	0.22	2.43	2.65	22.30	0.14	53
01-27-03	10.1	76	21.34	0.44	1.68	2.12	23.46	0.10	23
			24.80	0.40	2.08	2.49	27.29	0.11	

However, to accept the 2001-2003 results as correct and set up 1a as being able to capture and distinguish between gas phase and particle-bound formaldehyde, we need to address the four questions already mentioned. Let us deal first with the second question. DNPH-coated annular denuders have been reported to be highly efficient sinks (99%) for formaldehyde in air samples (Possanzini, *et al*., 1987). To confirm this report, key to our findings, we carried out efficiency tests in the laboratory at flows of 5, 10 and 15 L/min. A certified Teflon-membrane high diffusion tube (Vic Metronics, Inc, Santa Clara, CA) that yields 76.1 ng/min at 35ºC was used to provide realistic formaldehyde concentrations in the sampled air. This emission would produce formaldehyde concentrations of 15.22, 7.61 and 5.07 µg/m³, at 5, 10 and 15 L/min respectively. This flow was passed without humidification through two 25 cm long denuders connected in series during different sampling periods ranging from 30 to 240 min. Zero air was used as carrier gas. The sampling efficiencies (Eq. 1) are reported in Table 2. No replicate sampling was done, as the objective of this experiment was to confirm that a well-established methodology was applied correctly in our experiment. At short sampling times, the calculated efficiency is lower, possibly because of the low amount of formaldehyde trapped in the second denuder. The concentration levels detected were almost at the lower end of the calibration range.

$$E_s = \left[1 - \frac{D_2}{D_1} \right] \qquad (1)$$

Table 2. Laboratory sampling efficiencies of formaldehyde for the three-ring annular denuders used at different overall flow rates in zero air, using brand new denuders.

Sample time (min)	5 L/min	10 L/min	15 L/min
30	1*	1	1
60	1	1	1
90	1	1	1
120	> 0.99	> 0.99	0.98
240	> 0.99	> 0.99	

*All values equal one indicate a D_2 value lower than the detection limit.

Sampling efficiency was calculated using equation (1), where E_s is the sampling efficiency, D_1 is the mass trapped in the first denuder, and D_2 is the mass in the second denuder. The efficiency results shown in Table 2 could answer question two above. However, a study by Possanzini and Di Palo (1999) has shown that the sampling efficiency may depend on the relative humidity (RH). At 10 L/min, they observed a loss on efficiency at RH lower than 50%. At 30% RH, they concluded that the rate of formaldehyde removal to the denuder's walls was in the transition between the diffusion and the chemical kinetics limits. Therefore, the high efficiency we observed in our experiments with zero RH air needs to be conciliated with the RH effect observed by Possanzini and Di Palo. These differences could be explained by the geometry of the denuders. In their study, the denuders employed were 13 cm long, with 13 and 16 mm annulus diameters, which represent a 1.5 mm gap between the denuder's walls. The 25 cm long denuders used in this work have effective glass walls 22 cm in length, 70% longer. In addition, they contain several concentric tubes resulting in three concentric annuluses with a 1mm gap between the glass walls. This geometry divides the overall flow into three channels. The partitioning factor of the flow between each channel is the ratio of the given annulus area to the sum of the areas of the three annuluses. At an overall flow rate of 10 L/mim, actual flow rates through each annulus will be 2.27, 3.33 and 4.4 L/min from the inner to the outer annulus. How these differences may affect the overall sampling efficiency of the two different denuder systems?

Denuder's efficiency can be calculated using equation 2 (Possanzini and Di Palo, 1999):

$$E_s = a \ e^{-\lambda \Delta} \tag{2}$$

where:

$$\Delta = \frac{\pi \ DL \left(d_1 + d_2 \right)}{4f \left(d_2 - d_1 \right)} \tag{3}$$

Where D is the diffusion coefficient of formaldehyde in air (0.171 cm^{2}s^{-1} at 25 ºC); L is the length of the annulus; f is the flow through the given annulus in cm^{3}s^{-1}; d_1 and d_2 are the inner and outer

annulus diameters respectively. The empirical coefficients $\alpha = 0.94 \pm 0.11$ and $\lambda = 20.85 \pm 1.64$ with 90% confidence levels at RH of 60% (Possanzini and Di Palo, 1999). At 10 L/min, with the denuders used by Possanzini and Di Palo, the calculated efficiency was 0.89. The calculated weighed average efficiency of the denuders we used is 0.99. The weighing factor for each annulus is the ratio of its area to the sum of the areas of the three annuluses. For those denuders Δ is 0.10, whereas for any of the annulus in our denuders Δ is 0.66. This is almost a seven-fold increase in Δ, which in turn relates to the collision efficiency for the extinction on the walls. Therefore, lower actual flow rates through each annulus, longer annulus, and shorter wall-to-wall gaps will lead to a larger number of collisions able to compensate for the loss of collision efficiency due to lower RH.

To answer the first question, a Teflon filter was put under a flow of only 5 L/min of formaldehyde in zero air with a concentration of 15.22 mg/m^3 using the permeation tube described above. After four hours, a total mass of 18.26 μg of formaldehyde was permeated and passed through the filter. The filters were immediately extracted with the 0.1% DNPH-acetonitrile solution. This experiment was repeated four times. The average formaldehyde detected was 19.05 ± 6 ng, well within the field blank concentration. Therefore, we can conclude that Teflon filters do not trap formaldehyde and the flushed formaldehyde from the Teflon filters was not released from the filter material but from the trapped particles.

About the possible in-site formation of formaldehyde in the trapped particles (question 3), the most likely source of a positive formaldehyde artifact is ozone. KI coated denuders have been used in the past to scavenge ozone (Parmar and Grosjean, 1990; Vairavamurthy *et al.*, 1992). We observed that the scavenging efficiency of denuders coated with 10% KI drops to 40% after 30 minutes of exposure to a flow of 100 ppb of ozone in zero air. To be certain of their scavenging efficiency under field conditions, we tested them under conditions similar to those found in the experiments. Recently used 10% KI coated denuders were tested for efficiency at a flow of 10 L/min of 50 ppbv of ozone in zero air after humidification to 30% RH. They still showed a sustained scavenging efficiency of 95.4% ±1.6 % after four hours, the sampling period of all experiments in this work. The 1 km distant local air quality monitoring station (RAMA, Pedregal), reported average ozone ambient concentrations of about 10 ppbv from 8 to 10 a.m., then increased to an average of 70 ppbv at 12:00 a.m. In addition, the four hours average RH during the formaldehyde experiments ranged from 27 to 53%. Therefore, under field conditions ozone was scavenged with high efficiency by the 15 cm long KI coated denuders. On-filter production of formaldehyde due to oxidation of possible precursors can be ruled out as a source of the aldehyde extracted from the filters.

To answer question four we carried out from October 25 to 31, 2001, a short experiment. Four hours sampling from 8 to 12 a.m. was done on the roof of the Center for Atmospheric Sciences. These measurements were carried out under the same conditions as stated above, but the filter pack was displaced one stage forward from the ordinary set up (Fig. 1b). Two sampling strands were put on parallel. On completion of the sampling period, the filter packs were immediately sealed, taken to the laboratory and connected to a DNPH impregnated denuder to be flushed with zero air at 2 L/min for two hours one at the time. Table 3 shows the results: most of the formaldehyde is flushed out from the filter. In addition, the second filter, the one that had to wait, shows a large

drop of flushed formaldehyde. These results also support the assumption that formaldehyde is present in the suspended particles, and that a significant part of it is only weakly attached to this particles. Further reaction of formaldehyde to generate other products if not immediately flushed from the particles could also explain this observation in the second filter (Dultseva *et al.*, 2001).

Table 3. Mass (ng) of formaldehyde left in the filter and trapped in a DNPH coated denuder in the flushing experiment (see text).

Date	mF^{2*}	mD^{2*}	mF^{2**}	mD^{2**}
10-24-01	63.27	835.20	50.20	263.12
10-25-01	67.45	728.12	53.20	178.12
10-26-01	25.46	936.79	21.18	287.96
10-29-01	29.14	1023.96	27.15	318.14
10-30-01	27.65	916.52	20.65	232.17
10-31-01	20.18	864.47	13.65	102.40

mF^{2*} is the mass of formaldehyde left over in the filter after flushing from the first filter, mD^{2*} is the flushed formaldehyde from the first filter, mF^{2**} is the formaldehyde left over in the second filter that had to wait for the first one to finish, mD^{2**} is the flushed formaldehyde from the second filter

So far, we have given answer to the four questions that could cast a doubt on our conclusion that the sampling design depicted in Figure 1a is able to trap all the formaldehyde in air and to distinguish the phase distribution. However, if formaldehyde is so weakly attached to particles, could some formaldehyde found in D_1^1 be due to the loss from the particles as they travel along the first denuder, while the gas phase formaldehyde is already being scavenged on the DNPH-coated walls? This artifact will lead to an underestimation of the partition ratio. To answer this question we used three parallel sampling strands as in Figure 1 a, b, c. Table 4 shows the results.

Table 4. Concentrations (mg/m^3) of atmospheric formaldehyde in denuders and filter in the parallel experiments using setups 1a-1c in Figure 1. Includes escape efficiency from denuders in set ups 1b and 1c.

Date	Figure 1a				Figure 1b				Figure 1c			
	D_1^1	F^1	D_2^1	T^1	D_1^2	F^2	D_2^2	T^2	D_1^3	F^3	D_2^3	T^3
11-30-01	14.83	0.25	2.58	17.66	15.52	0.21	1.69	17.42	15.31	0.18	0.18	15.68
12-03-01	8.56	0.29	1.45	10.3	9.95	0.26	0.87	11.08	8.77	0.23	0.22	9.22
12-05-01	8.13	0.15	1.37	9.65	8.41	0.13	0.7	9.24	8.22	0.14	0.14	8.5
12-07-01	21.26	0.31	3.17	24.74	21.82	0.35	2.45	24.62	19.32	0.3	0.3	19.92
12-10-01	11.39	0.25	1.72	13.36	12.32	0.24	1.05	13.61	10.66	0.24	0.24	11.14
12-11-01	6.82	0.12	1.02	7.96	8.37	0.12	0.65	9.14	6.62	0.11	0.11	6.84
01-23-03	36.1	0.55	1.95	38.6	38.4	0.46	0.79	39.65	35.73	0.4	0.64	36.77
01-24-03	22.13	0.41	2.28	24.83	23.75	0.42	0.92	25.09	21.64	0.33	0.45	22.42
01-25-03	19.66	0.22	2.43	22.31	21.63	0.19	1.06	22.88	20.06	0.21	0.63	20.9
01-27-03	21.35	0.45	1.68	23.48	22.48	0.43	0.89	23.8	21.21	0.44	0.54	22.18
					*Mean E_E^2	0.07			Mean E_E^3	0.02		

If most of the formaldehyde in particles is only loosely bound to particles, and if equilibrium-shift (ES) and sample blow off (BO) are two physical processes that affect the apparent formaldehyde mixing ratios when sampling on the denuders + filter systems, then several hypothesis could be put forward:

1    $D_1{}^3 \approx D_1{}^1 < D_1{}^2 > D_1{}^3$

2    $F^3 < F^2 > F^1 > F^3$ (4)

3    $T^3 < T^2 > T^1 > T^3$

The hypotheses are checked using the Mann-Whitney non-parametric test with $p = 0.1$ to account for the small sample population (see Appendix). Nevertheless, notice that only test $T^2 > T^1$ requires such less stringent criteria instead of $p = 0.05$.

Results are given in Figure 2. The conceptual support for the hypotheses and a discussion of the results is given in the following paragraphs:

(i) Measurements in $D_1{}^1$ and $D_1{}^3$, would be subjected to the same conditions and the formaldehyde concentrations should be very similar. The null hupothesis ($D_1{}^1 = D_1{}^3$) should not be rejected. Measurements in $D_1{}^2$ should be higher than in $D_1{}^1$ and $D_1{}^3$ due to the BO artifact acting upon F^2. In addition, and extrusion effect (EE) to be discussed later, could also be present. The null hypothesis should be rejected for both comparisons. The three tests succeeded.

(ii) If the concentration of formaldehyde observed in the filters is under the influence of BO and ES then ES and BO would affect F^1 and F^3. Whereas F^2 would be affected by BO but not by ES ($F^2 > F^1$, $F^2 > F^3$), and F^3 by BO and by ES in a larger extent than F^1 ($F^1 > F^3$). The test failed for the first comparison. Also for the second (statistically significant differences but wrong direction) and succeeded for the third.

(iii) The total formaldehyde concentration observed in air ($T^j = D_1{}^j + F^j + D_2{}^j$) would be affected by sampling as follows: T^3 should be lower than T^1 ($T^3 < T^1$) and also than T^2 ($T^3 < T^2$) due to the lack of a third backup denuder after F^3 to trap the liberated formaldehyde due to the BO, ES and EE artifacts. T^1 should be lower than T^2 ($T^1 < T^2$) because of the EE artifact that only the Figure 1b set up can detect. The three tests succeeded.

Seven out of the nine hypotheses succeeded the tests. Let us now discuss the extrusion effect (EE). Table 4 also shows the escape efficiency E_E from the first denuder D_1 from set ups b and c in Figure 1, and those in Table 1, but now as given by equation 5:

$$E_E = \left[\frac{D_2}{D_1} \right] \qquad\qquad\qquad (5)$$

In Table 1, we compare the escape efficiencies for three different cases:

$(95, 0.471)\ D_1{}^3 \approx D_1{}^1 < (55, 0.001)\ D_1{}^2 > D_1{}^3\ (165, 0.001)$

$D_1{}^1/D_1{}^1,\ i = 1, 2, 3$

$(96, 0.47)\ F^3 < F^2 > (70, 0.009)\ F^1 > F^3\ (55, 0.001)$

$F^1/F^1,\ i = 1, 2, 3$

$(55, 0.001)\ T^3 < T^2 > (130, 0.063)\ T^1 > T^3\ (155, 0.001)$
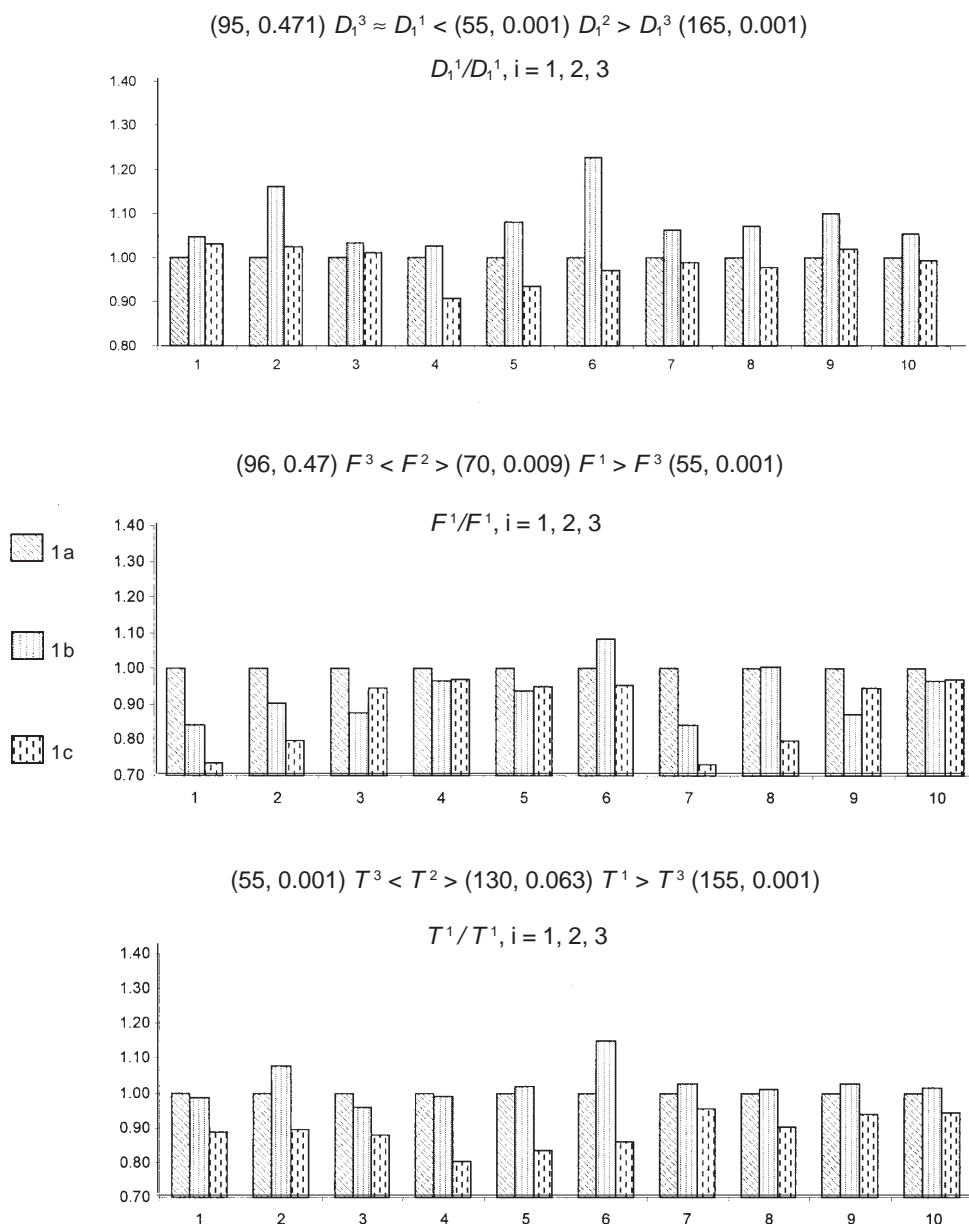
$T^1/T^1,\ i = 1, 2, 3$

Fig 2. Comparative results of the three different sampling setups and the associated hypothesis shown in equation 4 with the results accordingly to the Mann-Withney test with p = 0.1 as applied in the Appendix. Values within parentheses are (U, /p/). In all superindex: 1=1a, 2=1b, 3=1c as in Figure 1.

(i) A reference case; the escape efficiency in the laboratory experiment (E_L) carried out with a controlled flow of formaldehyde in zero air reported in Table 2.

(ii) The escape efficiency (E_E^2) in the field when the filter pack is put at the front (Fig. 1b).

(iii) The escape efficiency in the field (E_E^3) when the filter pack is put at the end of the sampling fence (Fig. 1c). For investigating the last two cases, we use the data in Table 4.

In comparing sampling efficiency (Eq. 1) on the laboratory against field measurements by set up Figure 1c, the sampling efficiency drops only 1%. However, seen as escape efficiency (Eq. 2) $E_E^3 = 0.02$ doubles in comparison with $E_L = 0.01$ when an undisturbed flow of polluted air with gas phase formaldehyde and formaldehyde in particles passes through the first denuder. This suggests that some formaldehyde in the particles is lost to the gas phase and trapped in D_2^3. ES seems to be the process leading to this observation after most of the gas phase formaldehyde is trapped in D_1^3.

When the filter is put in front of the sampling device (Fig. 1b), the escape efficiency E_E^2 is seven fold larger than E_L, and more than three times larger than E_E^3. So far, BO seems to be the only process acting upon the trapped particles in F^2. However, considering the already proven high sampling efficiency (E_L) with brand new denuders, there is not any apparent reason why E_E^2 is so high compared to E_L and E_E^3. This seems to suggest that very fine particles are able to pass through the Teflon filter (1 µm pore size), and that those particles will still be releasing formaldehyde to the gas phase after flying through D_1^2. A third backup denuder after D_2^1 would have been needed to detect that effect.

A comparison between E_E^2 and E_E^3 seems to suggest that those fine particles need to be "extruded" when forced to pass through the filter mesh to be able to release that formaldehyde. This would be the origin of what we call "extrusion effect". This process was already proposed in a not too different form by Klippel and Warneck (1980) to explain part of the formaldehyde observed in their backup filters.

4. Conclusions

Formaldehyde is present at relatively high concentrations in fine suspended particles in México City's aerosol. The sampling set up we propose in Figure 1a is able to distinguish the distribution of formaldehyde between the gas phase and $PM_{2.5}$. A considerable fraction of formaldehyde in suspended particles is weakly bound to them. In addition, part of the formaldehyde is weakly "shielded" in the finer particles. "Extrusion" of these fine particles, when passing through the filter mesh, enhances formaldehyde release to the gas phase when the phase equilibrium is displaced. These observations give place to serious questions about the possible role of suspended particles as a temporary sink of formaldehyde in photochemical smog. Such a source may modify the overall reactivity of photochemical smog. Questions about the actual potential exposure of the population to formaldehyde could be put ahead. Finally, if these observations can be applied to other light polar VOC our current view about the organic chemical composition of the $PM_{2.5}$ fraction may need to be broadened.

Acknowledgments

Appendix

Formally the Mann-Whitney test can not be used to test hypotheses as $A > B$, it is designed to test $A = B$. If we wish to test a hypothesis like:

$$A(a_1, a_2, \ldots a_n) > B(b_1, b_2, \ldots b_n)$$

with a one to one correspondence between a_i and b_i we need a work around. What we choose to do was:

$$C = A \cdot A^{-1}$$

$$D = B \cdot A^{-1}$$

where all $c_i = 1$.

Now apply the test for $C = D$. To accept the null hypothesis all or most of d_i should distribute evenly around $c_i = 1$. If there is a systematic preference for one side the test will fail, $C \neq D$, and that side will give the sense of the difference.

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