INVESTIGATIONS DURING SUMMER FIELD CAMPAIGNS IN CENTRAL EUROPE ON THE PERFORMANCE OF A DIFFUSION DENUDER FOR THE ELIMINATION OF SAMPLING ARTIFACTS FOR CARBONACEOUS AEROSOLS

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Keywords: filter sampling artifacts, diffusion denuder, carbonaceous aerosols, particulate mass.

INTRODUCTION

It is well-known by now that the collection of carbonaceous aerosols on quartz fibre filters suffers from artifacts (Turpin *et al.*, 2000; Mader *et al.*, 2003). Positive artifacts may occur by adsorption of volatile organic compounds (VOCs) to the filters and negative artifacts can occur by loss of semi-volatile organic compounds from the collected aerosol on the filters. It is thought that the positive artifact generally prevails. In order to eliminate the positive artifact, one can employ an appropriate denuder upstream of the filter collector. In a previous study, we examined the performance of a newly developed annular diffusion denuder (Mikuška *et al.*, 2003) during summer and winter sampling campaigns at an urban site, i.e., Gent, Belgium (Maenhaut *et al.*, 2003). Since the aerosol composition and the identity and concentration of the VOCs vary widely in time and space, the magnitude of the artifacts is expected to be highly dependent upon the sampling site and also upon the ambient conditions (such as temperature). In the current study, we examined the performance of the annular diffusion denuder during summer field campaigns at two forested sites in central Europe.

METHODS

The two forested sites in central Europe were Bily Kriz in the Czech Republic, near the border with Slovakia, and K-puszta in Hungary. At each site, two different PM2.5 filter samplers (both with 47-mm diameter filters) were operated in parallel at a flow rate of 17 L/min. DQ1Q2 had the newly developed diffusion denuder in between the PM2.5 inlet and the filter holder, which contained two quartz fibre filters in series. The denuder consisted of two sections, with a 22-cm long section of Na_2SO_3 on molecular sieve followed by a 65-cm long section of activated charcoal. Sampler Q1Q2 was identical to DQ1Q2, except that no denuder was used. All quartz filters were Whatman QM-A fibre filters, which had been heated overnight at 550°C to remove organic contaminants. At Bily Kriz, samples were collected from 31 May to 12 July 2003, the collection time per sample was typically 48 hours (starting in the morning), 21 parallel samplings were conducted, and 8 field blank collections were also done. The campaign at K-puszta lasted from 4 June to 10 July 2003, the collection time per sample there was typically 24 hours, 32 parallel samplings were conducted, and 13 field blank collections were done. PM was derived from weighing each filter before and after sampling with a microbalance. The filters were analysed for organic and elemental carbon (OC and EC) by a thermal-optical transmission technique (Birch & Cary, 1996).

RESULTS AND DISCUSSION

The median PM and OC concentrations (and ranges), as derived from the first filters of DQ1Q2 and Q1Q2 are presented in Table 1. The average concentration ratios (first filter of Q1Q2)/(first filter of DQ1Q2) and associated standard deviations were 1.40±0.18 and 1.16±0.11 for PM and OC, respectively, at the Bily Kriz site. The corresponding data at the K-puszta site were 1.49±0.24 and 1.42±0.11. Clearly, these ratios are substantially different from 1.00. Table 1 also gives the mean percentage OC on the second filter (relative to the first filter) at each of the sites (for PM there was a large uncertainty associated with its determination on the second filter). Also for the percentage OC on the second filter, substantial differences between DQ1Q2 and Q1Q2 exist. The differences for OC (and in part also these seen for PM) between the denuded and undenuded samplings have to be attributed to the presence of the denuder. While the percentage OC on the second filter of Q1Q2 is quite substantial at both sites, for DQ1Q2 very low percentages OC are found. This suggests that the denuder did retain all volatile organics and that there was virtually no loss of semi-volatile organic compounds from the collected aerosol on the first filters of the denuded samples. Mader *et al.* (2003) indicated that, if the positive artifacts prevail for the first filters in the undenuded samples and the negative artifacts for the first filters in the denuded samples, artifact-free OC data may be obtained for the undenuded samples by subtracting the OC on the second filter from that on the first filter, while for the denuded samples artifact-free data may be obtained by adding the OC data of the first and second filters. Moreover, the data from the two sampler types should be the same after applying such correction. By applying the correction, it was found that the average concentration ratio (first filter of Q1Q2)/(first filter of DQ1Q2) and associated standard deviation for OC were 0.95±0.12 for the Bily Kriz samples and 1.16±0.11 for the K-puszta samples. These ratios are clearly closer to 1.00 than the uncorrected ratios of 1.16±0.11 and 1.42±0.11. It seems thus that the above assumptions are valid for summer aerosol collections at forested sites in central Europe. Furthermore, at such sites and in summer reasonably accurate OC data may be obtained from undenuded samples by subtracting OC on the second filter from that on the first filter.

Table 1. Comparison of the PM and OC data from the various filters of two parallel samplers during 2003 summer campaigns at two forested sites in central Europe.

	Sampler DQ1Q2	Sampler Q1Q2
Concentrations in μg/m³		
	median (min. - max.)	median (min. - max.)
Bily Kriz		
PM on 1st filter	10.3 (5.6 - 14.2)	14.1 (8.1 - 18.8)
OC on 1st filter	2.62 (1.08 - 4.1)	2.98 (1.20 - 4.6)
K-puszta		
PM on 1st filter	12.5 (6.2 - 19.3)	18.2 (10.7 - 25.6)
OC on 1st filter	3.4 (1.43 - 5.5)	4.9 (2.09 - 7.6)
% OC on 2nd filter, relative to 1st		
	mean ± std.dev.	mean ± std.dev.
Bily Kriz	1.6 ± 2.2	16.7 ± 5.7
K-puszta	1.8 ± 3.2	16.9 ± 4.7

ACKNOWLEDGEMENTS

This work was supported by the Belgian Federal Science Policy Office (contract numbers EV/02/11A and BL/02/CR01), by a bilateral project between Flanders and Hungary, by the Hungarian Scientific Research Fund (Contr. T043348), by the Grant Agency of the Academy of Sciences of the Czech Republic (grant IAA4031105), and by the Grant Agency of the Czech Republic (grant GA CR 526/03/1182). We are also indebted to S. Dunphy for technical assistance.

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