Determination of Cr(VI), selected heavy metals, and elemental carbon in PM10 from a roadside sampling spot in Vienna

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Pollution from motor vehicles, in particular exhaust fumes and the wearing of disc brake pads, clutches, and tires, seems to be responsible for increased levels of heavy metals in particulate matter near roadside locations. Earlier studies have shown that, besides Sb and Fe, elevated levels of Cr also occur in particulate matter sampled near roadsides. In most cases, only total chromium, and not Cr(VI) levels are determined, which consequently provides only limited information about the toxicity and mobility.

The aim of the presented work was to assess the levels of selected heavy metals (Ba, Cd, Co, Cr, Cr(VI), Cu, Fe, Mn, Mo, Ni, Pb, and Sb) with the emphasis on Cr(VI). Furthermore, the origin of heavy metals was evaluated by calculating correlations with a marker for combustion engines, namely elemental carbon.

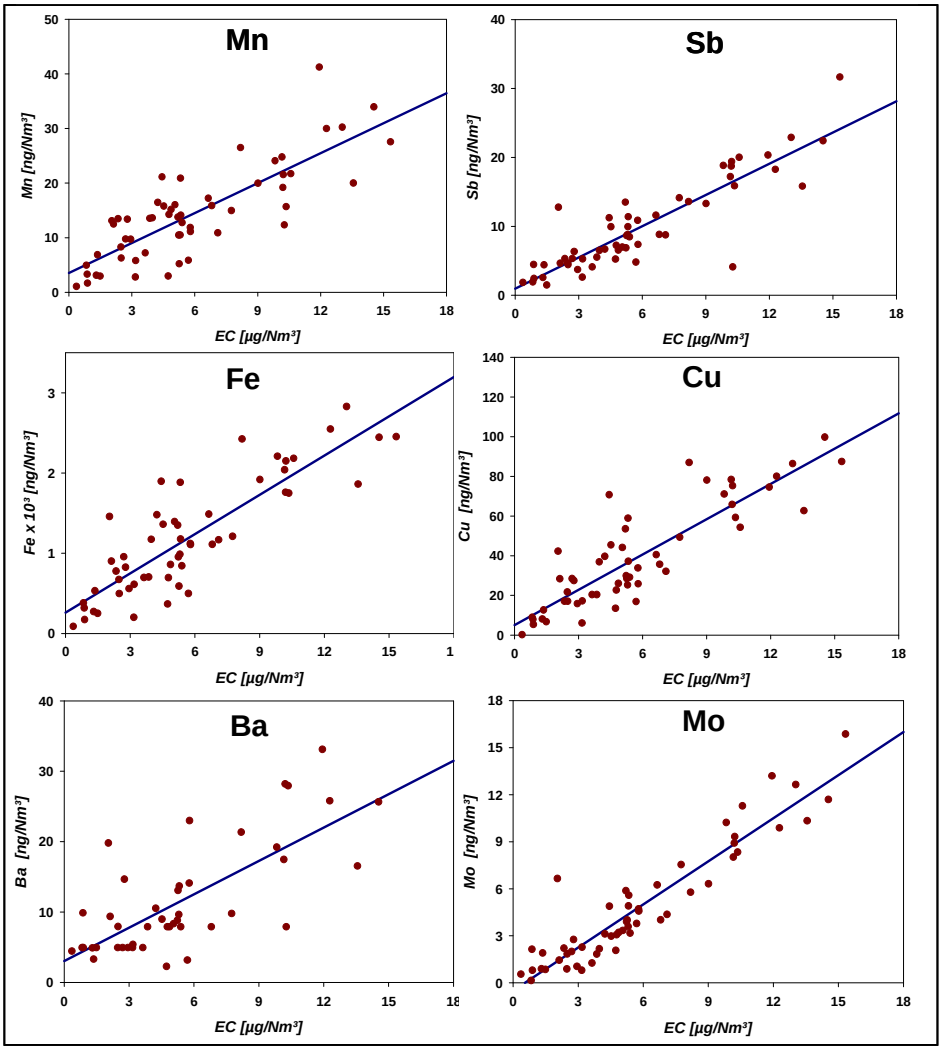

Fig. 1. Total element concentration of Antimony, Iron, Molybdenum, Manganese, Copper and Barium in correlation with elemental carbon level in the investigated PM10 filter samples.

For this purpose a sampling strategy with specially prepared quartz filters and appropriate storage conditions, combined with a straight forward and reliable sample preparation technique for the extraction of Cr(VI) in PM10 samples was developed. For the determination of Cr(VI), a chromatographic system with an anion-exchange column (Hamilton PRP-X100) was coupled to an ICPMS. Analysis time was less than 6 minutes and a LOD in the region of 50 pg/Nm³ was achieved. Quality control involved spiking the extraction solutions and the use of appropriate reference materials (BCR 545, welding dust loaded on filter). For total element analysis, the filter samples were digested with aqua regia via a microwave-assisted acid digestion. Elemental carbon was measured coulometrically after a Toluol/Isopropanol extraction step.

In addition to Sb, the elements Mn, Fe, Cu Mo and Ba showed a good correlation with the elemental carbon value (Figure 1). For the elements Pb, Cd, Co, Ni, as well as total Cr and Cr(VI), correlation with the elemental carbon was not observed. Values of all monitored heavy metals were in the µg/Nm³ region. Cr(VI) concentration did not exceed values of 1 µg/Nm³.

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Introduction

Pollution from traffic seems to be responsible for increased levels of heavy metals in particulate matter near roadside locations. Earlier studies have shown that numerous elements show elevated levels in particulate matter sampled near roadsides [1-3]. For Cr, only total but not Cr(VI) levels are determined, which consequently provides only limited information about the toxicity and mobility. The aim of the present work was to assess the levels of selected heavy metals with emphasis on Cr(VI). Furthermore, the origin of heavy metals was evaluated by calculating correlations with a traffic marker, namely elemental carbon (EC).

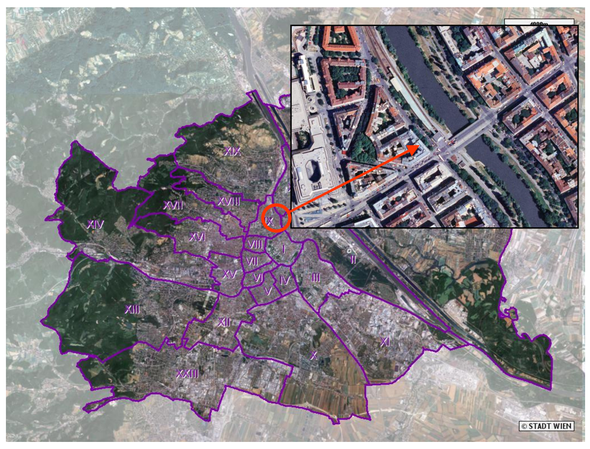


Fig. 1 Road map of sampling area

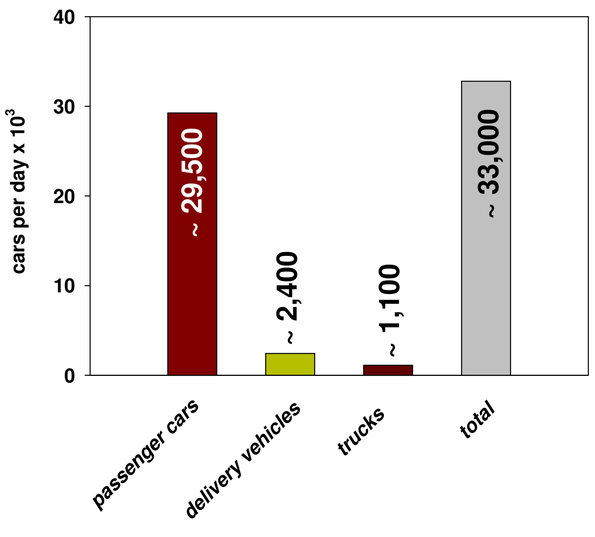


Fig. 2 Distribution of vehicle type at sampling spot

Experimental

Sampling was performed along a Viennese major road showing a traffic volume of more than 30,000 vehicles per day [4] (Fig. 1 & 2). Online measurements of the elemental carbon indicate two traffic peaks between 5^{00} and 9^{00} a.m. and 4^{00} and 7^{00} p.m. (Fig 3.). To evaluate the difference between

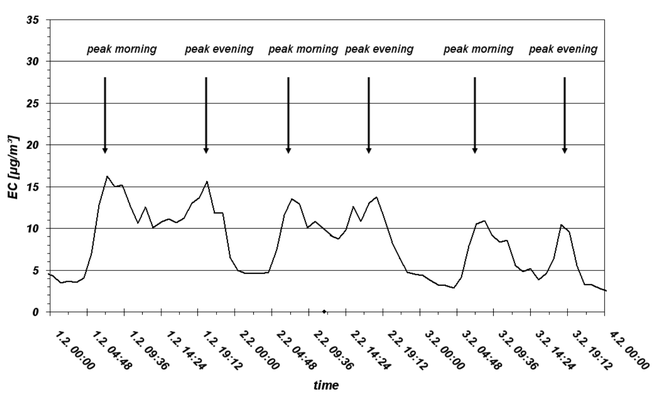


Fig. 3 EC emission versus sampling time

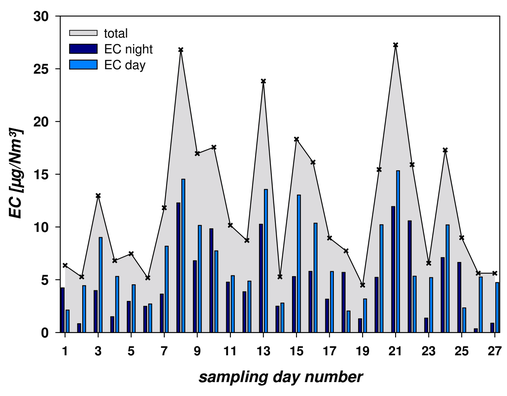


Fig. 4 EC values total, night, and day [µg/Nm³]

day and night traffic volume, sampling was split in two 12 hours intervals from 6^{00} a.m. to 6^{00} p.m. and 6^{00} p.m. to 6^{00} a.m. PM10 was colleted with a DIGITEL Aerosol DHA-80 high volume sampler on Whatman QMA quartz microfibre filters (∅ 15 cm, 2.2 µm immerged in NH_4HCO_3 [5]) for 27 days. Figure 4 shows day, night and total EC values of each sampling period.

Chromium speciation analysis was performed on a Perkin-Elmer LC200 equipped with a Hamilton PRP-X100 (2.1 x 150 mm) anion-exchange column. A 40 mM NH_4NO_3 /2% MeOH (v/v) solution served as mobile phase. A Perkin-Elmer ELAN DRCII ICPMS with NH_3 as reaction gas was used as element-selective detector. In Figure 5 a typical chromatogram of a PM10 filter sample is presented overlaid with a chromatogram of a 5 µg Cr(VI)/L standard solution [6,7].

***Total element* concentrations** were determined with ICPMS after an aqua regia microwave extraction procedure [8].

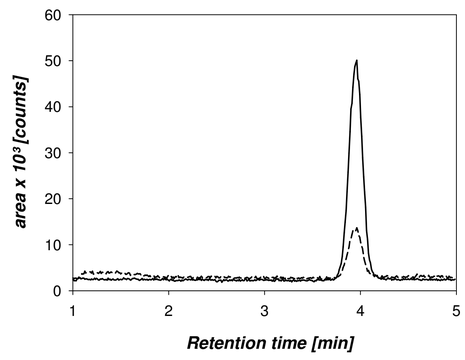
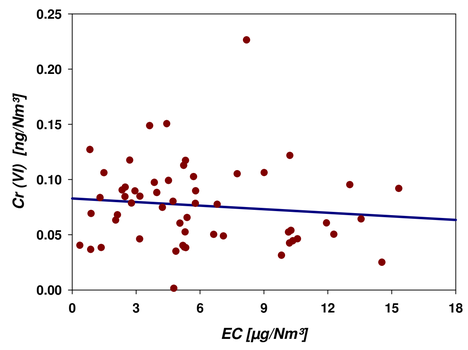


Fig. 5 Chromatogram of a PM10 sample overlayed with a 5 µg Cr(VI)/L Standard



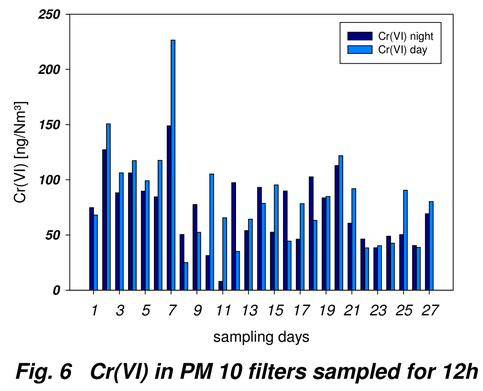


Fig. 6 Cr(VI) in PM 10 filters sampled for 12h

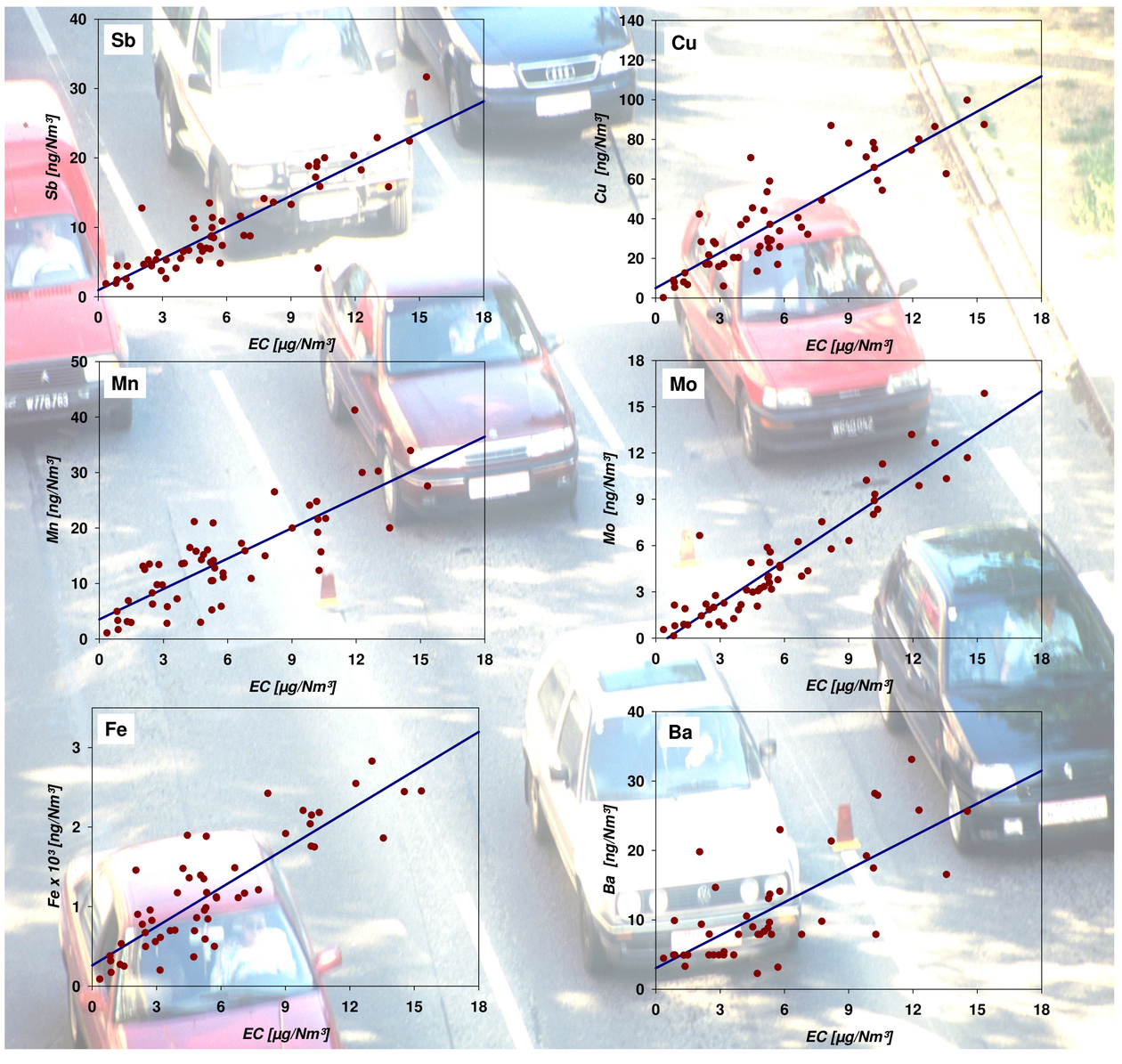


Fig. 8 Correlation of antimony, iron, molybdenum, manganese, copper, and barium vs. elemental carbon

Discussion

The developed method for Cr(VI) determination in PM10 does not require an intensive sample preparation, can be integrated into daily lab routine easily and delivers reliable results. During the sampling period Cr(VI) concentrations in PM10 filters (Fig. 6) were in the range of 0.04 to 0.23 µg/Nm³, which accounts for ~1% of the total Cr. Cr(VI) was not correlated with EC, a well accepted traffic marker (Fig. 7).

In contrast to Cr(VI) the elements Sb, Mo, Mn, Fe, Cu, and Ba showed a good correlation with the determined EC concentrations (Fig. 8) and seem to be mostly emitted by road traffic.

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