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Chemical and isotopic properties and origin of coarse airborne particles collected by passive samplers in industrial, urban, and rural environments

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HIGHLIGHTS

- ► Trace element data of coarse airborne particles collected with passive air samplers.
- ► Industrial and traffic sites are similarly affected by high atmospheric dust deposition rates.
- ► Isotopic tracers (Sr, Nd, Pb) and element triangle plots allow to identify polluting sources.
- ► Distinct atmospheric dust deposition events occur during the year.

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ABSTRACT

Passive air samplers have been installed in industrial, urban, rural and remote forested environments in order to collect coarse airborne particles for subsequent chemical characterization. To identify principal polluting sources, isotopic tracers, such as Sr, Nd and Pb isotopic ratios, have been used. The mass deposition rates (MDRs) of trace metals, determined for each of the studied environments, clearly indicate that industrial and traffic sites are especially affected by air pollution. Elements such as V, Pb, Fe, Cr, Co, Mo, Cd, Ni, As, Sb and Zn are notably enriched in samples from industrial zones, whereas V, Mn, Ba, Sr, Al, U, Th, rare earth elements (REE), Zr, Y, Cs, Rb, Sb, Sn and Cu are principal components of the airborne particles collected close to areas influenced by heavy traffic. The chemical/isotopic baseline composition derived from the airborne particles is the result of mixing of particles from different industrial sources, traffic and fertilizers. The monthly analysis of trace-metal MDRs of the collected airborne particle samples from different stations around the industrial zone allows for the detection of distinct atmospheric dust-deposition events during the year, characterized by high MDRs. "Natural" dusts from regional soil re-suspension, including from more distant regions like the Sahara desert, might overprint the regional atmospheric baseline composition, as suggested by trace metal trajectories in ternary diagrams and by Sr, Nd and Pb isotope data.

1. Introduction

Particulate matter (PM) is emitted into the atmosphere in fairly large quantities from industrial sites and vehicles (Kupiainen and Klimont, 2007; Winiwarter et al., 2009). It contributes to the degradation of the air quality and often induces significant health effects (Birmili and Hoffmann, 2006). The anthropogenic particles are added to the PM produced by natural mechanical disruptions (e.g. wind erosion, crushing, abrasion of surfaces, suspension and re-suspension of soil minerals, volcanic eruptions, dust storms). Apart from vehicle and industrial emissions, coal combustion (e.g. cooking, heating, power plants) represents an additional source of particulate air pollution in many countries (Chen et al., 2008). To improve air quality, one important task is to quantify the degree of air pollution by measuring the PM concentration and by identifying possible pollutants. Lead isotopic ratios have been shown to be a powerful tool to identify such sources (Bollhöfer and Rosman, 2001; Teresa de la Cruz et al., 2009) and to trace sources of organic pollution (Cheng et al., 2007). The concentration of Pb in air is still high in some places although the contribution from car exhausts is decreasing since the ban of leaded gasoline in 2000 (Teresa de la Cruz et al., 2009). Recent studies have shown that

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emissions from coal combustion, steel plants and waste incinerators cannot be traced exclusively by Pb isotopes but that they can be traced successfully with the help of Sr, Nd, Zn, Cd and C isotope ratios (Widory et al., 2004, 2010; Carignan et al., 2005; Lahd Geagea et al., 2008a; Díaz-Somoano et al., 2009; Shiel et al., 2010). Rare earth elements (REE) appear to be valuable tracers of refineries, petrochemical industries and steel plants (Kulkarni et al., 2006; Lahd Geagea et al., 2007; Moreno et al., 2008; Danadurai et al., 2011).

PM can be collected with active samplers, a method that is useful for the determination of the trace metal contents and isotopic composition of atmospheric PM (Lahd Geagea et al., 2008a; Moreno et al., 2008; Widory et al., 2010). In order to identify events of atmospheric pollution at a local scale (Widory et al., 2010), variations of elemental concentrations could be plotted as a function of time. An important disadvantage of active samplers, however, is that they need some additional accessories, such as, a power supply and air-flow meters, and, therefore, they are not very convenient for use in remote areas. In addition, the commonly used filter material can induce blank problems for concentration and isotope determinations on samples with especially low trace metal contents and/or low mass deposition. Most appropriate are PTFE filters (Lahd Geagea et al., 2008a), which, however, do not always allow for quantitative transfer of the sample for further chemical preparation because the particles can be strongly agglomerated by associated organic particles.

An alternative method for collecting ambient-aerosol particles is the passive sampler technique. Two types are in use, the "Sigma-2" sampler (VDI 2119, 2011) and the similar passive air sampler (PAS) used in atmospheric chemistry for the collection of organic pollutants (Wania et al., 2003). Both types of passive samplers have the advantage of being less heavy with no need of any power supply and thus, can be installed in many different environments, including very remote sites. The particles can be collected in a cleaned acceptor dish. Another advantage is that several of the comparatively low-priced passive samplers can be installed as a network, thus allowing for extended air quality monitoring. One important disadvantage of the passive samplers is the longer sampling time (1–4 weeks, depending on the environment), which is necessary to collect sufficient material for trace element and isotope analysis. Even with this rather long collection time it is not always possible to analyze both trace metal contents and isotope ratios. By contrast, active samplers allow for a much shorter sampling time of a few days. Thus, the passive samplers might integrate a much larger number of different chemical and isotopic signatures from various polluting sources than the active sampler, because they integrate over potentially changing wind directions.

The study presented here is the first using a wide network of Sigma-2 passive samplers exclusively for trace element and isotope measurements. The Sigma-2 passive sampler is primarily used for routine air quality measurements in German health and recreation resorts, which are licensed by state regulations and based on specific air quality standards (VDI 3787, 2010). In the almost wind-free interior of the sampler, particles are mainly deposited according to the sedimentation principle, largely eliminating deposition by turbulent diffusion (VDI 2119, 2011). Therefore, the special construction of the sampling device allows for coarse particle (>2.5 μm; Whitby and Cantrell, 1976; Gieré and Querol, 2010; VDI 2119, 2011; Grobéty et al., 2010) sampling with subsequent automated single-particle analysis by optical microscopy (Dietze et al., 2009) and calculation of particle-size distributions (VDI 2119, 2011). Apart from this routine application, the Sigma-2 technique is also in use for various air quality studies around the world (Schleicher et al., 2011, 2012). For the purpose of trace element and isotope measurements, a new collecting dish has been established in order to accumulate particles within the housing of the passive sampler device.

The aim of our investigation was to assess the air quality in the cities of Strasbourg (France) and Kehl (Germany), which are separated by the Rhine and located between the Vosges Mountains to the West and the Black Forest to the East. This area is especially well-suited for such a study, because various industries represent point sources for atmospheric pollution, including a steel plant (SP), a thermal power plant (TPP; wood combustion), a biomass heating power station (BHPS), a paper producer (PP), and domestic and chemical waste incinerators (DWI, CWI). At 18 sampling sites in the two cities and in the industrial harbors of Kehl and Strasbourg passive samplers have been installed for the collection of coarse PM over a period of one month to more than one year (SI Table S1). This long collection period allowed for monitoring of the air quality and detection of pollution events during this time. The air quality of this urban and industrial environment has already been assessed by tree-bark biomonitoring and trace element as well as isotope analysis (Guéguen et al., 2011, 2012a,b) and therefore, these data can be compared to the new air quality data presented here.

2. Material and methods

2.1. Sampling sites

The industrial harbors are in close proximity to the residential areas of Strasbourg and Kehl (represented in red and purple colors; Fig. 1). In order to characterize the different industrial emissions, dusts from electrostatic filters of the most important industrial facilities have been analyzed for their Sr, Nd and Pb isotopic composition and trace element contents (SI Tables S2 and S3). In addition, domestic chimney soot has been collected as a reference sample in order to obtain information about the chemical and isotopic composition of the particle emissions resulting from domestic wood combustion (SI Tables S2 and S3). Moreover, a surface-soil sample has been collected close to sampling site E (9 km to the North of the center of Strasbourg, see Fig. 1) in order to obtain information on the chemical and isotopic composition of soil dusts resulting from agricultural activities. Two samples of fertilizer have also been analyzed: fertilizer (I) has been used by farmers at sampling site E (Fig. 1) to the North of Strasbourg. Fertilizer (II) has been collected at the loading platform for fertilizers in the industrial harbor close to sampling site H3 (Fig. 1).

The main sampling sites for the coarse atmospheric PM are located in different parts of the industrial harbors (sites H1–H8) as well as in a private garden close to the industries (S3) (Fig. 1). Sampling sites were also set up in the urban areas of Strasbourg (S1–S5) and Kehl (K1–K2) as well as in the following areas near the two cities (Fig. 1):

1.) In the village of Auenheim situated to the Northeast of the steel plant (SP), representing the rural environment (A1).
2.) Two sampling sites were established for a limited duration at about 10 km north (E) and south (P1) of Strasbourg.
3.) In order to define the chemical and isotopic signatures of traffic emissions (mixture of gasoline and diesel soot and materials abraded from tires, brakes and road surface), PM samples have been collected close to a busy boulevard in Strasbourg (S2) and, for comparison, along a German highway in Freiburg (TR; SI Table S1; not shown on the map).
4.) The atmospheric background level was determined in the forested "Strengbach catchment" (BKG), located in the Vosges Mountains at an altitude of 1000 m a.s.l., 80 km to the South of the cities of Strasbourg and Kehl (Fig. 1) (Stille et al., 2011).