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Unraveling Pollutant Distributions on the Single-Particle Level: A New Aspect in Air Pollution Research

Introduction

Air pollution accounts for more than 6 million early deaths and 213 million years of healthy life lost worldwide in 2019, and is now listed as the 4th death-leading risk factor behind important chronic diseases including obesity, high cholesterol and malnutrition [1]. Among the different air pollutants, particulate matter (PM) represents the largest risk to human health, which is further increased by the rapid development of global industrial societies and the increasing number of wildfires in the course of climate change [2]. The detailed reasons and mechanisms of the observed PM health effects are still under investigation. The mass of inhaled PM-borne toxic substances is small if compared with the uptake of toxicants by ingestion, but the vulnerability of respiratory tract is driving the effects strength. The health effects strongly depend on the size and chemical composition of the particles. Ultrafine particles (Ø<100 nm, e.g. freshly formed particles) penetrate deep into the respiratory system and may enter the bloodstream [3] but carry only a little mass load of toxic substances into the body. Larger particles (Ø>2.5 µm, e.g. pollen) are typically deposited in the upper airways and bronchi. They are relevant e.g. for allergic symptoms (hay fever). The intermediate fine particle fraction (Ø>100 nm to 2.5 µm) can also reach and deposit in medium deep and the deepest lung regions (alveoli). These particles often contain high mass loads of toxic substances, overcoming the lung's cellular defense and leading to local inflammation – a starting point for serious health effects that are associated with cardiovascular diseases and cancer [4]. Also mechanically induced diseases, such as silicosis or asbestosis, are caused by persistent particles or fibers of this size range. Furthermore, the particle's long atmospheric residence times lead to an enormous chemical complexity due to atmospheric ageing. The particles are transported over long distances, posing an omnipresent risk even in less polluted regions [5]. Also natural fine dust levels are increasing due to desertification and storm patterns caused by climate change. Assessing the health effects from particles in the atmosphere, and the toxic compounds these particles can acquire during transportation over polluted regions, is still at its infancy [6]. The most relevant known toxic PM-compounds are on the one side redox-active or otherwise toxic metals such as lead, zinc or iron and on the other side cancerous polycyclic aromatic hydrocarbons (PAH) as well as their derivatives. Furthermore, the particles matrix itself (e.g. soot ~ elemental carbon, quartz ~ silicon dioxide, condensed organic matter) as well as the content of reactive oxygen species play a role. In addition to the epidemiological determination of the health effects, in-vitro and in-vivo model experiments are performed to understand the underlying mechanisms. In this context, new in-vitro approaches are under development using cell culture-based lung models for aerosol exposure at the air-liquid-interface (ALI) [7].

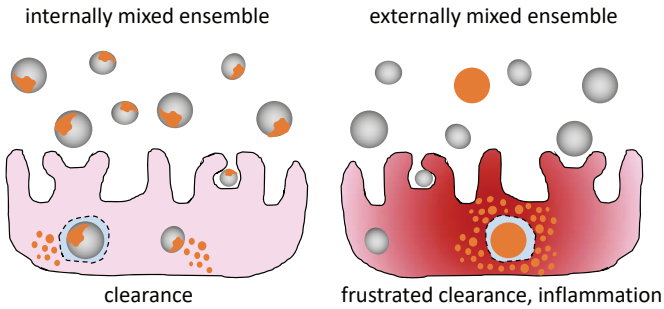

Fig. 1: Distributions of a toxic pollutant in a particle ensemble and their potential effects on lung cells or macrophages upon inhalation. Left: The uptake of many particles with low individual pollutant concentrations may be tolerated. Right: If few particles of the ensemble contain high loads of the pollutant, the cellular defense mechanisms might be overwhelmed, leading to adverse cytotoxic or genotoxic effects. Note that the integral pollutant concentrations of both particle ensembles can be equal, e.g. as measured form an aerosol filter sample. This illustrates the need for single-particle analytical approaches.

These ALI experiments enable realistic PM exposure scenarios and are still reproducible enough to allow systematic experimental studies. Recent studies have shown that e.g. the toxicity of ship emission depends on the fuel quality [8] or that secondary organic aerosol formed during photochemical ageing from anthropogenic precursor gases is more toxic than from biogenic precursors [9, 10]. Further studies shall investigate the multiple interaction pathways of lung epithelial cells or macrophages with individual particles on the microscopic scale. The cells actively or

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passively take up particles (phagocytosis), ingest toxic PM compounds from the lung lining fluid or sense PM-surface structures via receptors. These processes can lead to adverse molecular processes, finally manifesting in cytotoxic or genotoxic outcomes. The emerging research question of sophisticated understanding of the particle-cell interaction and the molecular mechanisms on the cellular level also challenge the chemical PM characterization. The conventional aerosol analysis methods describe integral compositions, i.e. the observed toxicant content is averaged over all collected particles and size fractions. Thus, they cannot capture the distribution effects of pollutants in the particle ensemble. According to the microscopic concept of the particle-cell interaction (Fig. 1), the distribution of toxicants within the particle ensemble (i.e. the so-called internal/external mixing) is of high importance. However, only few singe-particle methods resolving the mixing state are available. Most of them are based on electron microscopy with integrated element analysis and can assess only small particle numbers with limited chemical speciation, e.g. by XRF. The second approach is single-particle mass spectrometry (SPMS), a real-time method providing a chemical fingerprint of individual particles. Novel SPMS concepts now enable the simultaneous single-particle resolved detection of the most toxicological relevant pollutants: PAH and metals.

Single-Particle Mass Spectrometry (SPMS)

As discussed before, an important aspect is the mixing state of a given pollutant over the particle ensemble (Fig. 1), which is inherently addressed by the particle-by-particle characterization in SPMS [11, 12]. Herein, individual particles are exposed to intense laser pulses, and thus, both positive and negative ions are formed by laser desorption/ionization (LDI) and detected in a bipolar MS setup. Common ionization products are cations of metals, salts, carbon clusters from soot or ammonia. Most molecules are fragmented, thus the plethora of organic pollutants is missed in conventional SPMS.

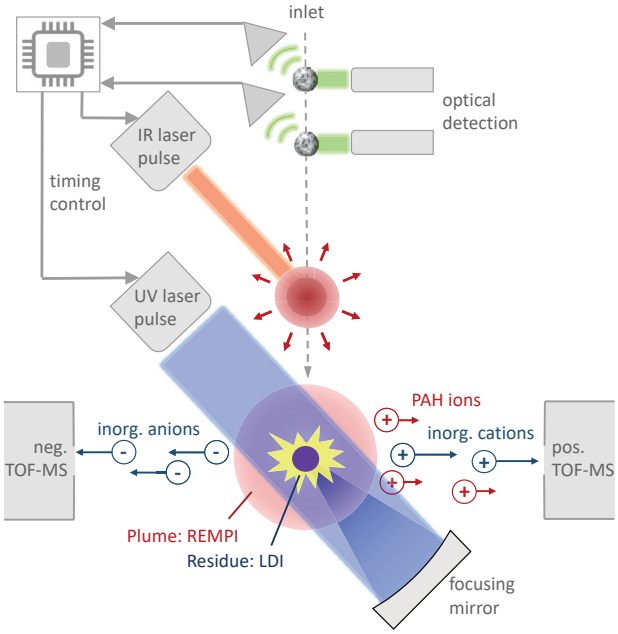

Fig. 2: Schematic of a SPMS setup with novel particle ionization method. Particles are accelerated in a vacuum expansion and detected via laser velocimetry (green lasers). The novel ionization method is based on a sequence of tailored pulses: An IR pulse producing an expanding gaseous plume which is intersected by a delayed UV-pulse for REMPI of PAHs. The UV pulse is back-reflected and focused into the refractory particle residue in the plume center, exceeding the intensity threshold for LDI of inorganic particle components. Ions of both polarities are detected in a bipolar MS setup.

Simultaneous Single-Particle Detection of Polycyclic Aromatic Hydrocarbons and Metals

PAHs are toxic trace components in aerosols with additional direct climate forcing and indirect climate effects, e.g. via photooxidation and cloud condensation [13]. Despite years of research, little is known about the detailed distribution pathways and their complex atmospheric interactions [13]. We developed new laser ionization methods for SPMS that produce full-fledged mass spectra of PAHs from individual fine and ultra-fine particles – in addition to the inorganic composition with, e.g., toxic metals [14]. Key of the method are spatially and temporally matched laser pulses that simultaneously induce two different

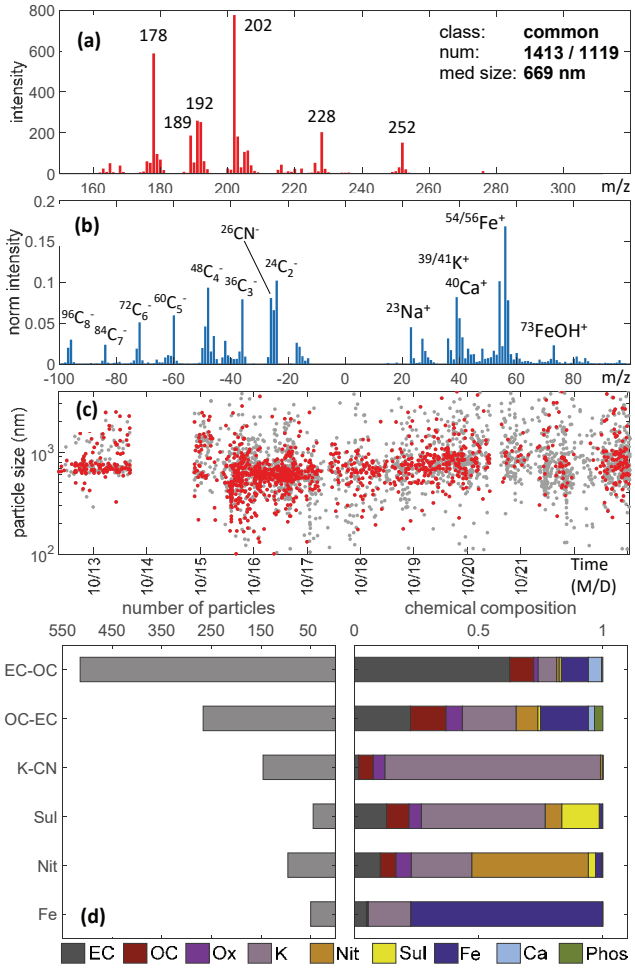

Fig. 3: (a) Spectrum of the most abundant PAH signature (1,413 particles, whereof 1,119 show additional LDI mass spectra). (b) Averaged LDI mass spectra of this cluster. (c) Occurrence of these particles (red dots) within the measurement period (x-axis) and their size (y-axis). Grey dots: other PAH-containing particles. (d) Left panel: number of particles in the subgroups with respect to their inorganic composition. Here, particles mixed of elemental carbon (EC, from soot) and organic carbon (OC) from traffic and wood combustion dominate. Particles with high loads of secondary sulfate and nitrate, e.g. from coal combustion, marine life and agriculture, are less often associated with this PAH profile. Figure from [15].

ionization pathways, see Fig. 2. The flying particle is hit in the vacuum of the instrument by an infrared laser pulse that desorbs non-refractory components and produces an expanding gas plume. Few microseconds later, the plume is intersected by an ultraviolet laser pulse of moderate intensity for fragment-free and ultra-sensitive resonance-enhanced multiphoton ionization (REMPI) of the PAHs in the plume. The same laser pulse is back-reflected and focused using a concave mirror and hits the residual particle core in the center of the plume with much higher intensity, forming anions and cations of inorganic compounds by LDI simultaneously to the REMPI-generated PAH ions. The ionization of PAH (REMPI, desorption plume) and metals (LDI, particle core) is thus spatially separated. With this new method, the distribution of PAHs on different particle types in ambient air could be investigated for the first time [15]. The field study at the Swedish coast revealed long-range transport of wood combustion and traffic-related particles from Central and Eastern Europe (Fig. 3). Moreover, signatures of PAH degradation, mixing and ageing of organic components were observed in a complex real-world aerosol, introducing the ultra-sensitive PAH-detection as a molecular sensor approach for atmospheric processes.

Enhanced Single-Particle Detection of Metals by Resonant Laser Desorption/Ionization

Inhaled particles containing transition metals such as iron (Fe) induce oxidative stress and are involved in both acute and long-term health effects from air pollution [16]. Furthermore, metal-containing aerosols are important sources of marine micronutrients controlling primary production and carbon fixation in large parts of the world's oceans [17]. We tune UV laser pulses from an optical parametrical oscillator (OPO) to ground state transitions of the target elements. Consequently, metal atoms that were released from the particle in the leading edge of the laser pulse are excited and can thus undergo single-photon ionization [18]. This approach largely enhances the sensitivity of SPMS for these relevant aerosol components. In particular, the highly abundant and redox active element iron is of interest, both for its health effects and its role in biogeochemical cycles in the earth system [17]. With the UV-laser wavelength of 248.3 nm, we address the $3d^64s^2 \rightarrow 3d^64s4p$ Fe-transition and induce REMPI of PAHs, which allows to combine the detection of PAHs with enhanced sensitivity for the detection of iron. For field applications, the Fe atomic and PAH molecular resonances can be addressed by a KrF-excimer laser. In an exemplary field study, we thus could shed a light on the Fe carriers in a complex aerosol at the Swedish coast, see Fig. 4 [18]. Beyond air pollution monitoring and health related aerosol studies this method paves a new way to elucidate the sources and transport pathways of bioavailable metals to the oceans [18, 19].

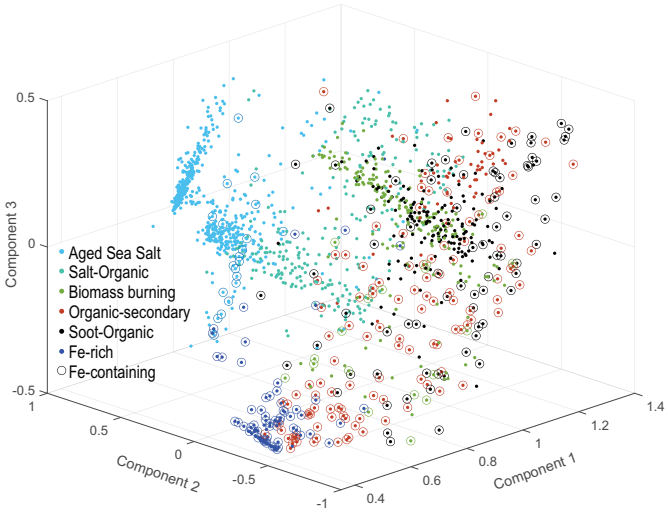

Fig. 4: Principal component analysis of chemical profiles from individual aerosol particles, measured at the Swedish coast and classified by a neural network (ART-2a). Exploiting laser-atom resonances, the method discloses the dominant Fe-carriers (circulated), here industrial/traffic combustion potentially affecting marine life and human health. Also mixtures with sea salt contribute to the Fe transport [18].

Conclusions and Outlook

The mixing state of aerosol particle constituents is a largely unconsidered aspect of the ambient aerosol, albeit important impacts for the mixing state on e.g. aerosol toxicity, micronutrient transport and condensation nuclei properties are anticipated. The further development and an increased application of SPMS with novel multi-step laser ionization schemes will close important research gaps, enabling a new perspective on complex ambient aerosols and their role in climate and human health effects. In addition to scientific applications and environmental monitoring, the improved SPMS technology may also be developed towards process monitoring applications or real-time ambient air surveillance for the detection of hazardous emissions.

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