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Identification of non-regulated polycyclic aromatic compounds and other markers of urban pollution in road tunnel particulate matter

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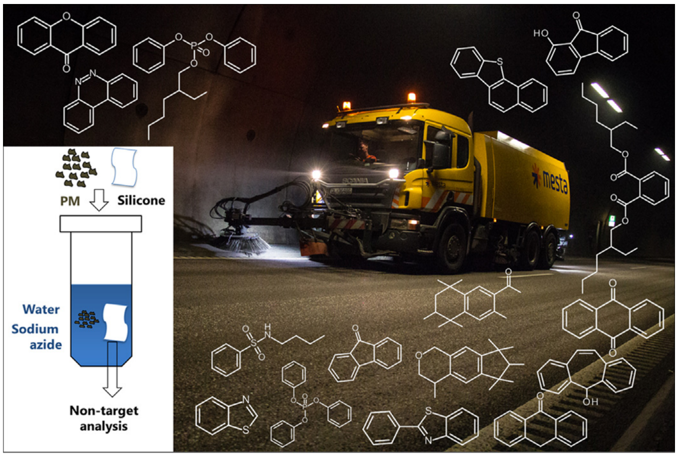
HIGHLIGHTS

- Silicone rubber extracted a broad range of compounds from tunnel particulate matter.
- 90% of the compounds identified by non-target screening were PACs.
- A major portion of the PACs were alkylated and/or contained a heteroatom.
- Urban markers were also identified by non-target and suspect screening.
- Co-chromatography with authentic standards confirmed the identity of 16 compounds.

GRAPHICAL ABSTRACT



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ABSTRACT

A combination of silicone rubber extraction and non-target and suspect screening by gas chromatography coupled to high-resolution time-of flight mass spectrometry was used for the identification of compounds in particulate matter (PM). Tunnel PM is a proxy for local road pollution that constitutes a hazard to the urban environment and human health. The use of silicone rubber for the extraction of PM allowed the pre-concentration of a wide range of compounds for non-target analysis while minimising the effects of the sample matrix. As expected, polycyclic aromatic compounds (PACs) constituted the major group of compounds identified, but only 5 of 50 PACs identified were amongst those regularly monitored and many of them were alkylated or contained a heteroatom. Urban markers of contamination such as organophosphate flame-retardants, phthalates, benzothiazoles, musk compounds and a plasticiser were also identified. The level of confidence for the identifications was high based on accurate mass, the pattern of fragmentation and retention. The unequivocal identification of 16 compounds, from all groups, was confirmed by co-chromatography with standards and the compounds semi-quantified. Most of the PACs identified are not regularly monitored, and the hazards they pose are therefore unknown. Some of these PACs are known to be more persistent and mobile in the environment than the EPA PAH16.

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1. Introduction

Our society and economy are dependent on the transport of goods and personal mobility with road transport a key component of an integrated transport policy [1]. However, roads are pervasive in modern landscapes and may be detrimental to the environment. For example, road runoff has been recognised for its environmental hazard potential since the early 1970s, while the discharge of severely contaminated tunnel wash water has been only recently investigated [2]. Assessment of the environmental risk posed by road runoff has to date been mainly focused on salt, hydrocarbons, polycyclic aromatic hydrocarbons (PAHs) and certain metals such as cadmium, copper lead, nickel and zinc [3]. In the past years, there has been a substantial reduction in exhaust emissions from road traffic due to the regulation of emissions [4]. At the same time, non-exhaust emissions such as particles from brake pad and tyre wear as well as road surface abrasion are still unabated [5]. Tunnel PM has been used as a matrix to make source apportionment of traffic emissions of PM [6], demonstrating that toxic metals and PAHs showed high incremented levels. Deposited PM inside tunnels can be viewed as an aspect of local road pollution, since the majority, if not all of the pollution, comes from traffic and the already mentioned sources [6], as well as technical infrastructure such as traffic signs, guardrails, electrical- and light gear. Long-range transport of compounds is thus eliminated, and therefore tunnel PM is an interesting matrix for identifying the specific chemicals that constitute an environmental threat to the local environment.

Non-target screening is a suitable technique for detecting the presence of a large number of compounds and a broad range of groups in environmental matrices. The search for unknown chemicals in the environment typically involves high resolution mass spectrometric analysis of samples obtained following exhaustive extractions of environmental matrices [7,8]. The technique has arisen as the result of the increased availability of high-resolution mass spectrometry (HR-MS). Such instrumentation is utilised in a number of different fields such as metabolomics, drug discovery, forensic toxicology, anti-doping and environmental research. Highly sensitive accurate-mass measurements over a full mass spectrum make it possible to screen for a large number of organic contaminants at reasonably low levels. The confidence of identifications resulting from non-target analysis can vary, depending on whether confirmation by complementary methods has been performed. Consequently, evaluations of the level of confidence identifications by HR-MS has been proposed [9–11]. One advantage of acquiring full scan MS data is that they remain available for later analysis. Subsequently, suspect screening can be performed by obtaining narrow mass windows of extracted ion chromatograms (nw-XICs) at abundant ions of the compound in question.

We have recently shown that the combination of passive sampling and non-target screening is a powerful technique for assessing the presence of compounds that are potentially bioaccumulative or "mobile" [12]. Passive sampling is a suitable sampling technique for moderately polar and nonpolar substances, and the contaminants that absorb into silicone rubber are typically non-ionised and hydrophobic substances. This selectivity can help reduce the amount of clean-up of the extract required following elution of all chemicals absorbed into the samplers. The selection of passive sampling material can also influence the types and classes of chemicals that can be sampled, which was demonstrated in our previous study where organophosphate compounds accumulated to a larger extent in silicone rubber than low density polyethylene (LDPE) passive samplers [12]. This is not surprising since silicone rubber has the highest permeability of most polymers [13]. For example, higher contaminant diffusion coefficients have been measured for substances such as organophosphate compounds or polybrominated diphenyl ethers in silicone rubber than in low density polyethylene (LDPE) [14]. Generally the *ex-situ* extraction of contaminants from PM such as sediments with a passive sampler involves measuring either the activity of the contaminant of interest or its desorbable concentration, both measurements being useful tools in risk assessments [15].

A limited number of compounds have been investigated in road runoff and the hazard potential of this urban matrix is at present mainly based on only the concentrations of metals and PAHs. In line with what has been demonstrated for other PAH sources such as oil and coal tar pitch, the monitored EPA PAH16 only represent a minor part of the compounds present and the toxic potential [16,17]. Our goal was to employ non-target screening to identify compounds present in the particulate phase of road runoff. A combination of silicone rubber accumulation with non-target techniques had proven useful for identification of contaminants in surface water [12]. We consequently wanted to explore the suitability of silicone rubber as means of extracting PM as part of our investigation. A tunnel PM sample was therefore subjected to analyses by both non-target analysis and suspect screening to investigate additional compounds to what is normally analysed for that are present in an important urban matrix.

2. Materials and methods

2.1. Particulate matter (PM) collection and characterisation

The samples investigated by non-target screening in this paper are part of a larger set of road-impacted PM investigated for PAH availability through silicone rubber extraction [18]. The sample for which detailed non-target results are described here is an aliquot of the sweeper sample from the Nordby tunnel described in that article (sample D). Several of the other samples were also injected on the GC/HR-MS-ToF instrument and data recorded, but a thorough; non-target screening has only been attempted for the single sample described here.

The PM sample was collected in November 2013 directly from a road-sweeping vehicle during a scheduled road tunnel wash in the Nordby tunnel system, located along E6 30 km outside of Oslo, Norway. The tunnel is typically washed an average of five times a year, and the sweeping is done directly before washing. The Nordby tunnel system is 3.8 km long and consists of two tunnels with two driving lanes in each tunnel. The walls and the roof of the tunnel are covered with concrete, while the road surface is asphalt. The traffic intensity is approximately 32,000 vehicles/day (ca. 11% heavy goods vehicles) and the speed limit is 90 km/h. The amount of PM collected by the road sweeper annually is approximately 15 t [19]. A 2 kg sample of PM was then placed in an air-tight container at −20 °C until solvent extraction (2 months storage) and silicone rubber extraction (4 months storage).

Laser granulometry and Rock-Eval analyses were performed to characterise particle size distribution and organic carbon content of the PM. The PM sample was relatively coarse with a large proportion of particles with diameter greater than 100 μm. The total organic content was low (1%) and the proportion of refractory carbon was just under 40% indicating that much of the organic carbon present in this sample comprise a significant amount black carbon-type material.

2.2. Materials

All glassware was either solvent rinsed or baked at 550 °C. Solvents were from Rathburn (Walkerburn, Scotland) with the exception of cyclohexane (J.T. Baker, Deventer, Holland) and were of HPLC grade or better. Analytical-grade standards for deuterated PAHs were from Chiron (Trondheim, Norway). The standard

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