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Leaf-deposited semi-volatile organic compounds (SVOCs): an exploratory study using GCxGC-TOFMS on leaf washing solutions

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Abstract

Airborne particulate matter (PM) includes semi-volatile organic compounds (SVOCs), which can be deposited on vegetation matrices such as plant leaves. In alternative to air-point measurements or artificial passive substrates, leaf monitoring offers a cost-effective, time-integrating means of assessing local air quality. In this study, leaf washing solutions from ivy (*Hedera hibernica*) leaves exposed during one-month at different land use classes were explored via comprehensive two-dimensional gas chromatography with time-of-flight mass spectrometry (GCxGC-TOFMS). The composition of leaf-deposited SVOCs, corrected for those of unexposed leaves, was compared against routinely monitored pollutants concentrations (PM_{10}, $PM_{2.5}$, O_3, NO_2, SO_2) measured at co-located air monitoring stations.

The first study on leaf-deposited SVOCs retrieved from washing solutions, herein reported, delivered a total of 911 detected compounds. While no significant land use (rural, urban, industrial, traffic, mixed) effects were observed, increasing exposure time (from one to 28 days) resulted in a higher number and diversity of SVOCs, suggesting cumulative time-integration to be more relevant than local source variations between sites. After one day, leaf-deposited SVOCs were mainly due to alcohols, N-containing compounds, carboxylic acids, esters and lactones, while ketones, diketones and hydrocarbons compounds gained relevance after one week, and phenol compounds after one month. As leaf-deposited SVOCs became overall more oxidized throughout exposure time, SVOCs transformation or degradation at the leaf surface is suggested to be an important phenomenon. This study confirmed the applicability of GCxGC-TOFMS to analyze SVOCs from leaf washing solutions, further research should include validation of the methodology and comparison with atmospheric organic pollutants.

Keywords

Biomonitoring • Ivy leaves • Semi-volatile organic compounds • Leaf deposition • Two dimensional gas chromatography • Time-of-flight mass spectrometry

1. Introduction

Among air pollutants, particulate matter (PM), ground-level ozone (O_3) and nitrogen oxides (NO_x) are generally recognized as the most health-threatening air pollutants (EEA, 2008), yet volatile organic compounds (VOCs) are of growing concern as they are involved in the formation of secondary organic aerosols and can be adsorbed to aerosol particulates (Bessagnet et al., 2010). Organic matter contributed substantially to both outdoor (ca. 29%) and indoor (ca. 54%) fine PM concentrations in 173 USA homes (Polidori et al., 2006). Both PM and organic species are associated with oxidative stress and subsequent inflammatory responses (Bernstein et al. 2004). Within VOCs, the subgroup of semi-volatile organic compounds (SVOCs) is of relevance, as these compounds are frequently detected in particulates and various surfaces. In a subtropical urban area in Taiwan, semi-volatile materials (comprised by SVOCs and NH_4NO_3) were accounted for 25% of the $PM_{2.5}$ aerosol mass (Salvador and Chou, 2014). SVOCs typically have higher molecular weight and boiling point in comparison to VOCs, so they volatilize relatively slower (at standard temperature and pressure conditions) than the latter. SVOCs include a multiplicity of pollutants such as polycyclic aromatic hydrocarbons (PAHs), organochlorine pesticides (OCPs) and polychlorinated biphenyls (PCBs) (He and Balasubramanian, 2010a, 2010b). PAHs mostly derive from incomplete combustion (e.g. fossil fuels, forest fires), OCPs from vegetation and soil spraying, and PCBs, although banned during the 80s (directive 96/59/EC), are still released by a variety of materials (e.g. plastics) (Colman Lerner et al. 2016). Many SVOCs are considered to be toxic, mutagenic and potentially carcinogenic, as well as to have endocrine-disrupting effects both in animals and humans (Dallongeville et al. 2016; Kummer et al., 2008; Santodonato, 1997). The main human exposure pathways comprise inhalation of vapor- and particle-bound SVOCs, dermal absorption and non-dietary ingestion (via household dust) (Weschler and Nazaroff, 2008, 2012; Xu and Zhang, 2011).

After release to the atmosphere, SVOCs are generally partitioned between gaseous and particle-bound phases, depending on their vapor pressure and temperature dependences (Atkinson, 1991;

Pankow, 1994). Processes such as revolatilization, atmospheric transformation (e.g. degradation by ultraviolet rays), exchange between air and water (Herbert et al., 2006; Larsson et al, 1992; Parnis and Brooks, 2000), air and soil (Cousins et al., 1999; Cousins and Jones, 1998), or air and vegetation (Simonich and Hites, 1995; Orecchio, 2007; Wang et al., 2015) also contribute to the fate and transfer phenomena of SVOCs within the environment. Monitoring methodologies of SVOCs can be done by active sampling or through a variety of synthetic passive samplers (e.g. diffusion tubes). In addition to that, vegetation matrices (such as plant leaves) have been recognized as valuable sensors for monitoring environmental contamination (e.g. Bakker et al. 2001) being particularly useful for detecting pollution hotspots. In terms of availability and ease of maintenance on-site, monitoring strategies by means of plant leaves offer several advantages. Plants are typically widespread enabling low-cost leaf sampling at high spatial-resolution; whereas in more isolated locations, plant leaves are more expeditious to obtain in comparison to air samples. Although plants with distinct leaf morphology (e.g. surface area, roughness, presence of trichomes) and anatomy (e.g. stomata density, presence and composition of cuticular waxes) perform differently in terms of capture efficiency, accumulation of pollutants on leaves is a function of air concentrations (Calamari et al., 1991; Simonich and Hites, 1995; Wannaz et al., 2013). A library of studies is presently available on the use of plant leaves as reliable sensors for a variety of health-threatening air pollutants such as trace metals, PM and PAHs (e.g. Cocozza et al., 2016; Hofman et al., 2017; Lehndorff and Schwark, 2004, 2010; Sawidis et al., 2011). Yet studies exploring the range of SVOCs deposited on urban leaves are still scarce, almost uniquely targeting PAHs captured by pine needles species (Baráková et al., 2017; Piccardo et al., 2005; Ratola et al., 2014; van Drooge et al., 2014). The exchange of SVOCs between air and vegetation involves primarily (dry) gaseous deposition and (wet and dry) particle-bound deposition, while uptake via root systems or wet deposition of dissolved species are assumed to be negligible for most cases (McLachlan, 1999; St-Amand, 2009a, 2009b). The relative occurrence of those two key mechanisms is related to the gas-particle partitioning and volatility of the compound, with particle-bound deposition becoming more relevant with decreasing volatility. Moreover, SVOCs can be transferred from the atmosphere (by gaseous/particle-bound deposition) onto the waxy cuticle of plant leaves or by uptake through their stomatal cavities (McLachlan, 1999).

Methodologies to study SVOCs retained onto plant leaves, as well as by most synthetic matrices, very often include a solvent extraction step using e.g. toluene or acetone (Esteve-Turrillas et al., 2012), which is laborious and environmentally aggressive. Also, intensive clean up steps are required after extraction due to sample contamination with leaf material compounds. Our monitoring study of leaf-deposited SVOCs aimed for a simple, more environmentally responsible extraction approach, by hand washing the surface of exposed leaves in order to retrieve the fraction of leaf-deposited pollutants. These leaf washing solutions were explored via comprehensive two-dimensional gas chromatography with time-of-flight mass spectrometry (GCxGC-TOFMS) to evaluate potential signatures of leaf-deposited SVOCs accumulation and how this accumulation may differ between the considered land use classes. The objectives of this study were defined as follows: (a) to investigate the suitability of GCxGC-TOFMS applied to leaf washing solutions as an exploratory tool for leaf-deposited SVOCs, (b) to examine the evolution of leaf-deposited SVOCs over time and across study sites attributed to different land use classes, and (c) to evaluate possible relationships between leaf-deposited SVOCs and regularly monitored atmospheric pollutants (namely, $PM_{2.5}$, PM_{10}, NO_2, SO_2 and O_3) measured by the official air quality monitoring network. The accumulation of SVOCs on leaf material depends on atmospheric concentrations, environmental and meteorological conditions and plant properties (McLachlan, 1999). Therefore, to get a representative insight into SVOCs accumulation, plants of one single species were monitored during ca. one month.

2. Materials and methods

2.1 Leaf monitoring and sampling

Ivy (*Hedera hibernica)* plants, approx. 130 cm in height and grown along vertical bamboo sticks, were obtained from a nursery (Agora Group, Kontich, Belgium) and planted in allpurpose potting soil, inside robust plastic boxes (polypropylene; 43 cm x 36 cm, 26 cm height). Each box, which was pierced with holes to enable drainage, contained six plants in 25 L of potting soil, of which one plant was selected for this study. The boxes with the plants were then placed outdoors at seven study sites, i.e. in the enclosure of seven selected air quality monitoring stations maintained by the Flemish Environment Agency (VMM) in the province of Antwerp, Belgium. Two boxes were placed per monitoring site. The study sites were attributed to different land use classes (Table 1), including industrial, rural, traffic and urban land use, according to the definition used by VMM. The site *Borgerhout* (*BH*; traffic) is close to a high traffic intensity road, *Groenenborgerlaan* (*G*; urban) is located in a more residential area with traffic, and Park Spoor Noord (*P*; urban) in an urban park. *Boudewijnsluis* (*BW*; industrial) is located in the harbor where petrochemical industries prevail, while *Hoboken* (*H*; industrial) is located rather near a metal-emitting factory. The land use class of one of the study sites, *Luchtbal*, (*L*) was however defined as mixed, as the site is under the influence of urban and traffic conditions and close to industry (ca. 2 km) and harbor infrastructures (ca. 700 m). The site *Dessel* (*D*; rural) is situated in a rural area, i.e. a more background location, but traffic from boats and motorized water sports is still present in the nearby canals. All study sites (further illustrated in Figure A.1) were located within a 9 km radius from Antwerp city center, with the exception of *Dessel*, which is located at ca. 50 km from Antwerp. Plants were placed at the study sites on December 8, 2015.

At each study site, a total of ten healthy, undamaged ivy leaves were collected at day one (1d), seven (7d) and 28 (28d) after exposure, on December 9 and 15, 2015, and January 5, 2016, respectively. Leaf samples were also taken one day prior to exposure (December 7, 2015). Per box, five leaves of comparable size were chosen from a selected plant and cut with scissors using gloves. In order to avoid contamination by possible soil resuspension, the leaf sampling height was in the range 50 - 120 cm above ground level, which also corresponds to the breathing height range of young children. The ten leaves collected per site were stored together in paper envelopes and kept in the fridge (4 °C) before analysis.

2.2 Preparation of leaf washing solutions

Within three days after sampling, the collected leaves were hand-washed individually by rubbing them gently using nitrile powder-free gloves (VWR International, Radnor, USA) during 1 min each in a total of 800 mL of ultrapure water (0.5-1 µS cm^{-1}) (Silex 1B ST3, Eurowater, Eke, Belgium). The leaves were rubbed at both sides (adaxial and abaxial, each side for 30 s). This procedure was followed with the intention to retain in the washing solutions the SVOCs that were adsorbed onto the leaf surface or bound to leaf-deposited particulates, after the findings of He and Balasubramanian (2010b). In that study, the (particulate-associated and dissolved) concentrations of SVOCs in rainwater samples exhibited a trend comparable to the atmospheric SVOCs (particle and gaseous phases) concentrations, thus showing the potential of water solutions to capture and collect such compounds. The (one-sided) leaf surface area of the washed leaves, measured with a leaf area meter LI-3100C (Licor Biosciences, USA), was on average 26.2 ± 9.3 cm^2 (n = 280) per leaf. The obtained washing solutions were stored in rinsed glass bottles (1 L), labelled and kept in an acclimatized dark room at 16 °C, before being transported to the lab of Water-Link in Rumst, Belgium, for GCxGC-TOFMS analysis. Leaves collected one day prior to exposure were submitted to the same sample preparation procedure and the obtained leaf washing solutions were used as blanks. In total, 28 leaf washing solutions (from the seven study sites, sampled on three point-time measurements and prior to exposure) were analyzed.

2.3 GCxGC-TOFMS analysis

A fully automated method has been set up for analyzing the leaf washing solutions via GCxGC-TOFMS. This analysis was performed within five days after leaf washing. Fifty mL of each sample was concentrated using a Spark Symbiosis System (Spark Holland BV, Emmen, NL) on a cleaned Hysphere Resin GP cartridge. After rinsing and drying, the cartridge was eluted with 100 µL ethyl acetate (Pesti-S, Biosolve Chimie, Dieuze, France), from which 20 µL was injected on a cold PTV injector (Optic 3, Atas Gl, NL). Each sample was then separated on a FactorFour VF-1ms (30 m x 0.25 mm x 0.25 µm) coupled with a FactorFour VF-17ms (1 m x

0.1 mm x 0.20 µm) (Agilent J&W) using a slow gradient (60 min total analysis time) on a 6890 GC (Agilent Technologies, Palo Alto, USA). The compounds were measured on a Pegasus 4D (Leco Corporation, St. Joseph, USA) and m/z ratios between 33 and 450 amu were collected at 100 spectra/s. Peak detection was automated and the peaks were cleaned by deconvolution. Mass spectral database search to identify the detected organic compounds was conducted based on the NIST Mass Spectral Library (NIST/EPA/NIH, v2, 2011). Peak tables from the blank samples, i.e. the leaf washing solutions prepared with unexposed leaves, were compared manually against the peaks of the samples, and all compounds present simultaneously in the sample and in the corresponding blank were neglected. This was done individually for the seven study sites.

2.4 Air quality and meteorological data

Concentrations of atmospheric particulate matter, with particle aerodynamic diameter below 10 µm (PM_{10}) and 2.5 µm ($PM_{2.5}$), were determined in the seven air monitoring stations by using an optical particle counter (Fidas 200, Palas, Germany) and a conversion to mass concentration. Gaseous pollutant concentrations, namely ozone (O_3), nitrogen dioxide (NO_2) and sulfur dioxide (SO_2), were measured at some of the air monitoring stations (see Table 1), via UV-photometry (API T400, Teledyne, USA), chemiluminescence (TS 42i, Thermo Scientific, USA) and UV-fluorescence (TS 43i, Thermo Scientific, USA), respectively. Daily mean concentrations of PM_{10}, $PM_{2.5}$, NO_2, SO_2 and O_3 are shown in Figure A.2 and A.3.

Meteorological data were available at the *Luchtbal* monitoring station. The prevailing wind directions during leaf exposure were SW and S with an averaged wind speed of 18 (± 6) km h^{-1}. For the same period, the mean daily temperature and relative humidity were 10 °C (± 2 °C) and 87% (± 5%), respectively, while total cumulative precipitation was 41.8 mm with major rain events on December 11, 2015 (9.8 mm) and January 3, 2016 (11.2 mm). The precipitation between sampling dates was 1.6 mm (1d), 13.8 mm (7d), and 26.4 mm (28d).

Table 1 – Location and land use class of the seven study sites, and indication of the air pollutants measured at the co-located air monitoring stations.

Study site	Geographic coordinates	Land use class	Air pollutants measured
Borgerhout (BH)	51°12'33.95"N 4°25'54.08"E	Traffic	$PM_{2.5}$, PM_{10}, NO_2, SO_2, O_3
Boudewijnsluis (BW)	51°16'51.38"N 4°19'47.50"E	Industrial	$PM_{2.5}$, PM_{10}
Dessel (D)	51°14'01.2" N 5°09'50.6"E	Rural	$PM_{2.5}$, PM_{10}, NO_2, SO_2 and O_3
Groenenborgerlaan (G)	51°10'38.17"N 4°25'4.64"E	Urban	$PM_{2.5}$, PM_{10}, NO_2
Hoboken (H)	51°10'12.99"N 4°20'27.39"E	Industrial	$PM_{2.5}$, PM_{10}, NO_2, SO_2
Luchtbal (L)	51°15'39.41"N 4°25'27.78"E	Mixed	$PM_{2.5}$, PM_{10}, NO_2, SO_2
Park Spoor Noord (P)	51°13'44.93"N 4°25'33.83"E	Urban	$PM_{2.5}$, PM_{10}, NO_2,

2.5 Data analysis

The detected organic compounds were corrected for with those from the non-exposed leaves, but no internal standard compounds were used to calculate the extraction recovery or to aid in the detection of targeted compounds. The methodology herein used consisted thus in an exploratory, non-target screening, with supervised identification of the organic compounds done on a similarities/dissimilarities basis (similarity of the mass spectrum with that of the NIST Library was at least 700/1000). The mass spectral data obtained with GCxGC-TOFMS allow compound classification into groups having comparable chemical properties (e.g. m/z 57 is a characteristic peak for alkanes), however, it is not always possible to unequivocally identify individual compounds due to the nature of electron spectra, as electron impact ionization often leads to the loss of the molecular ion (Vogt et al., 2007; Welthagen et al. 2003). For this reason, the identified organic compounds were not ascribed to a specific chemical formula, but classified into 23 compound groups depending on their prevalent functional group (namely, alcohols, aldehydes, alkanes, alkenes, aromatics, carboxylic acids, cyclic ethers, diketones, esters, ethers, furans, hydrocarbons, ketones, lactones, N-containing compounds, phenols, polyalcohols, polyaromatics, polyethers, polyether alcohols, sugars, terpenes, and other). The category *Other* comprises all organic compounds from poorly represented categories, i.e. from groups with two or less detected compounds.

Output chromatographic data included the 1st and 2nd dimensions, m/z unique mass, peak area and signal-to-noise (S/N) ratio, for all detected peaks. Whenever multiple peaks were identified as originating from the same compound, the S/N ratio from those peaks was summed together and the obtained, total S/N ratio was then considered. Focusing on the most abundant present compounds, a spectral intensity dataset according to the S/N ratio of all detected compounds was produced. The distribution (in %) of those organic compounds into the defined compound groups was also considered, and the diversity of the organic compounds in each sample calculated as the number of compound groups present.

Given the large and complex nature of the dataset, a principal component analysis (PCA) was performed on the S/N ratio of all detected organic compounds, using JMP Pro 13 (SAS Institute Inc., 2015). To evaluate relationships of SVOCs composition with atmospheric key pollutants, the sample scores along the first two axes of the PCA (PC1 and PC2) were tested (using linear model fits) against the routinely monitored pollutants concentrations (PM_{10}, $PM_{2.5}$, O_3, NO_2, SO_2) at the co-located air monitoring stations. The number of organic compounds, as well as the PC1 and PC2 scores, were also tested for exposure time (linear model fit), study site and land use class (Kruskal Wallis test) effects. The pollutants concentrations (PM_{10}, $PM_{2.5}$, O_3, NO_2 SO_2) were checked in terms of temporal behavior through pairwise Kendall correlations, as well as for study site and land use class effects using analysis of variance (ANOVA) and Tukey HSD tests. To evaluate whether variations in the composition of the organic compounds, for the considered study sites and exposure time, can be explained by differences in the air pollutants concentrations measured at the co-located monitoring stations, Kendall correlations were calculated between the matrix of Euclidean dissimilarity in organic substances (*vegan* package; Oksanen et al., 2017) and the differences in air concentrations, with Mantel tests (10,000 permutations) using the R software package (R Core Team, 2017). In this type of test, the distance matrix between the analyzed samples (dependent variable) is compared with the distance matrix between certain environmental variables (predictor variable) (e.g. PM_{10} concentration on the day of sampling) by permuting rows and columns of the first, to check if samples submitted to similar environmental conditions also tend to be similar in terms of the dependent variable. In the present study, the geographic distances among study sites and atmospheric PM_{10}, $PM_{2.5}$, O_3, NO_2 and SO_2 concentrations (on leaf sampling day, averaged from two days prior to that and cumulatively since exposure) were tested as predictors of leaf-deposited SVOCs composition.

3. Results and discussion

3.1 GCxGC-TOFMS on leaf washing solutions: exploratory tool for leaf-deposited SVOCs?

Comprehensive GCxGC with TOF-MS detector is often used for analyzing complex matrices such as aerosol samples, where most organic compounds occur in low concentrations (Hamilton et al., 2004; Vogt et al., 2007), but also when first exploring a novel sample type, as is the case for leaf washing solutions. For the latter, a non-target screening is particularly relevant as it permits the detection of all present compounds. In this experiment a total of 911 different organic compounds were identified from the analyzed leaf washing solutions, which appears to be in accordance with related studies done on ambient air. In a set of urban air samples from Melbourne, Australia, Lewis et al. (2000) found and classified more than 500 organic compounds using GCxGC. Welthagen et al. (2003) observed a minimum of 15,000 peaks on daily $PM_{2.5}$ quartz fiber filters, collected in Augsburg, Germany, with 65% of the isolated compounds effectively assigned to compound groups, thus enabling a rather direct characterization of the constituents of ambient PM. Even though the organic compounds resolved in this study should not be directly compared against those obtained from forced-air collectors (e.g. filters), they are a result of atmospheric pollutants accumulated on the leaves' surface. The water-removable fraction of leaf-deposited pollutants has been studied before to highlight the main contaminating sources (e.g. Fernández Espinosa et al., 2002; De Nicola et al., 2008). Two distinct biomagnetic studies of plane tree leaves done in Antwerp included unwashed and water hand-washed leaves to investigate leaf deposition and encapsulation of magnetic particles (Hofman et al. 2014a, 2014b), which are known to be invariably linked to anthropogenic PM pollution. The water-removable fraction (i.e. unwashed leaves – washed leaves) contributed on average to 62% (Hofman et al. 2014b) and 66% (Hofman et al., 2014a) of the total leaf magnetic signal. De Nicola et al. (2008) had also reported that most of the particle-bound trace metal elements in *Q. ilex* leaves were removed after water-washing them by shaking alone. In the same study, total PAH concentrations from the washed leaves were not significantly different than those obtained from the unwashed leaves though, which was hypothesized as due to PAHs migration into the leaf wax layer after deposition (De Nicola et al., 2008). The presence of a large number of organic substances in our washing solutions, corrected for the organic substances of unexposed leaves, suggests that leaf washing solutions can be useful environmental indicators *per se*. According to Simonich and Hites (1995) and references therein, the use of plant leaves as accumulators of organic atmospheric pollution can constitute a valid qualitative mechanism to estimate their contamination levels as long as certain aspects influencing the plant uptake mechanisms are taken into consideration. These include plant species and leaf lipid content, time of exposure, ambient air temperature, air pollutant concentration, particle-gas partitioning, hydrophilicity or lipophilicity of the compound. The experimental design herein reported considered plant leaves, from similar age and background, from the same species (and so, with comparable lipid content) with similar exposure time and meteorological conditions for all study sites, while the other parameters are mainly depending on the polluting compounds present on-site, thus, on the local sources and conditions.

3.2 Leaf-deposited SVOCs over time and across different land use classes

With exception of sites *P* and *L*, the number of detected organic compounds showed to increase with exposure time (Table 2). The lowest number of organic compounds were observed after one day, i.e. 38 and 39 compounds at sites *P* and *BH*, whereas a maximum of 289 SVOCs was registered after 28 days in the *BH* site. *BH* site is located at ca. 7 m from a traffic-intensive road (Plantin en Moretuslei) with on average 29,500 vehicles per day (VMM, 2014), which may explain the steep increase in the number of SVOCs throughout exposure. At this study site, the number of organic compounds detected over the entire exposure time increased by a factor of ca. 7, while this increment, between day one and day 28, was in the range of 2 to 3 times for all other sites. After 28 days of exposure, the sites *BH* (traffic), *BW* (industrial) and *G* (urban) revealed more than 180 different leaf-deposited organic species each, but these values did not show a considerable difference when compared to the rural site *D*, which is assumed to be more protected from pollution sources. A higher, until 30-times, PAHs accumulation has been measured in (dichloromethane: acetone based-extracted) *Q. ilex* leaves from urban areas compared to those in remote areas (De Nicola et al., 2011). However, the lowest number of compounds after 28 days of exposure was detected at the urban park site *P*. A linear model fit regression confirmed that the number of detected SVOCs increased with the exposure time (R^2 = 0.52, $P < 0.001$), while no significant differences were detected between the considered study sites nor land use classes ($P = 0.88$ and $P = 0.98$, respectively).

Table 2 - Number of detected leaf-deposited SVOCs and of compound groups thereby represented, in the analyzed leaf washing solutions per study site (BH – Borgerhout, BW – Boudewijnsluis, D – Dessel, G – Groenenborgerlaan, H –Hoboken, L – Luchtbal, P – Park Spoor Noord) and exposure period (1d, 7d, 28d).

	# detected SVOCs			**# compound groups**		
Exposure / **Study site**	1d	7d	28d	1d	7d	28d
Borgerhout (BH)	39	142	289	13	16	21
Boudewijnsluis (BW)	62	131	185	13	15	20
Dessel (D)	50	114	148	11	18	17
Groenenborgerlaan (G)	92	112	194	17	19	21
Hoboken (H)	49	49	135	10	12	18
Luchtbal (L)	61	139	125	14	20	17
Park Spoor Noord (P)	38	143	111	11	17	16

The overall increase in the number of SVOCs with longer exposure time was followed by an increase in diversity, as a larger number of compound groups was observed after seven and 28 days of exposure than after one day (Table 2). For all samples the most detected functional compound groups were N-containing compounds (17%), carboxylic acids (14%), esters (10%), ketones (9%), and alcohols (8%). A rapid visualization of the GCxGC-TOFMS contour maps (see Figure A.4) also points out to an increase over time in the number and diversity of compounds. This temporal evolution of the leaf-deposited SVOCs can better be evaluated in terms of their distribution into chemically-related groups (Welthagen et al., 2003) (Figure 1). Most detected leaf-deposited SVOCs after one day are categorized as alcohols, N-containing compounds, carboxylic acids, esters and lactones, whereas ketones, diketones and hydrocarbons compounds appear to gain more relevance after seven days of exposure. For most study sites, the largest variety of compound groups was found at the end of the monitoring campaign, i.e. after 28 days. Moreover, the contribution of phenol compounds in all study sites showed to be the largest for those 28 days' samples.

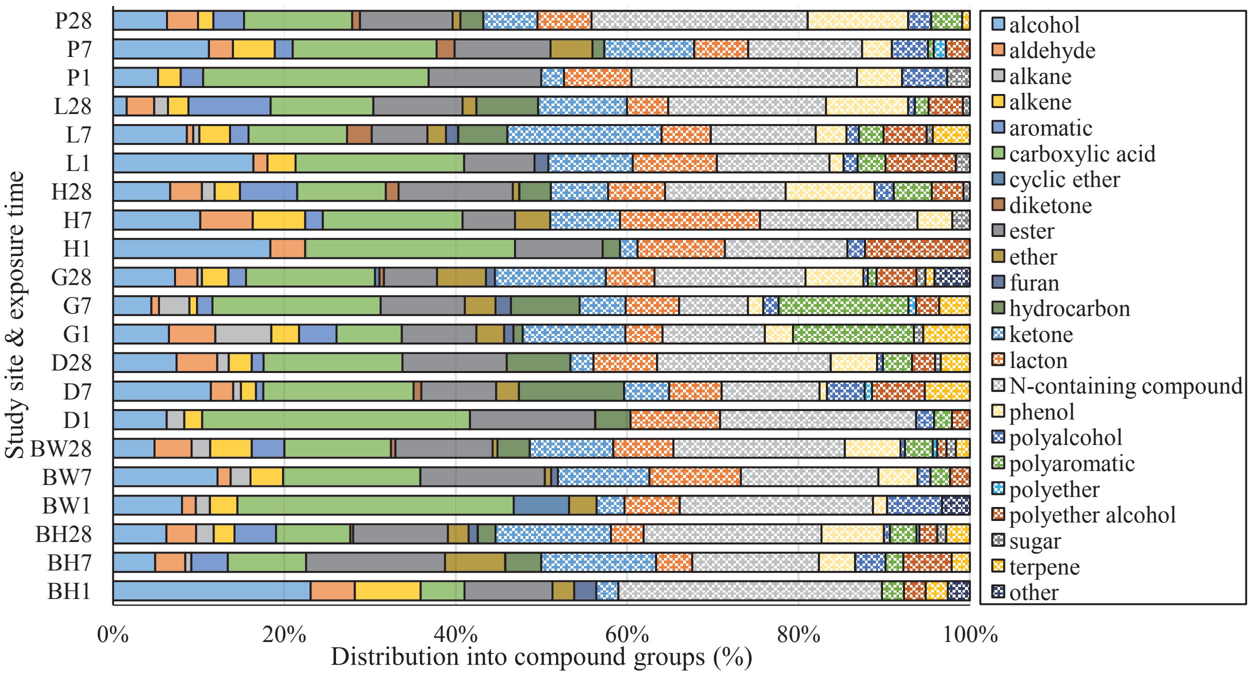

Figure 1 – Distribution (%) of the organic compound groups represented within the leaf washing solutions per study site (BH – Borgerhout, BW – Boudewijnsluis, D – Dessel, G – Groenenborgerlaan, H – Hoboken, L – Luchtbal, P – Park Spoor Noord) and exposure period (1, 7, 28 days).

The results of this first experiment using leaf washing solutions showed that leaf-deposited organic compounds become in general more oxidized with increasing exposure time. This can be observed when e.g. comparing the higher contribution of ketone compounds in the samples exposed for seven days, than in the samples exposed for only one day (see Figure 1). The presence of alcohols, one of the most easily oxidizable functional groups in organic chemistry, decreased from one to 28 days of exposure, suggesting further oxidation processes to happen over time. Also for most sites, aldehyde compounds, often formed after the oxidation of alcohols, showed a higher occurrence in the samples of seven and 28 days when compared to the samples of one day of exposure. On the other hand, this is not corroborated by the distribution of carboxylic acids, which are a good model for highly oxidized compounds as they are obtained after oxidation of aldehydes, over exposure time. A possible explanation for the latter may be that those carboxylic acid compounds, already oxidized in the aerosol matrix or originated from the oxidation of leaf-deposited aldehydes, could not oxidize up to other organic compounds after leaf deposition.

Even though not possible to be tested statistically, the exposure period appears to be a key factor in the composition of leaf-deposited SVOCs, which suggests that, at least a part of, the airborne organic compounds remain active after the process of leaf deposition. Degradation of atmospheric SVOCs occurs naturally due to photolysis or reaction with atmospheric reactive species such as O_3, hydroxyl radicals and NO_2 (Melymuk et al., 2014; Weschler and Nazaroff, 2008), and is not only described for plant and leaf surfaces (Simonich and Hites, 1995), but also for filters and impaction plates (Schauer et al., 2003). It can thus be hypothesized that during almost one month of exposure, some degradation phenomena have occurred at the leaf accumulated SVOCs. On the other hand, no major differences or trends were identified on the distribution of SVOCs between the considered study sites. Therefore, the increasing oxidation state of the leaf-deposited SVOCs over time seems most likely related to the compounds' transformation and/or degradation than to possible variations in the emission sources from the considered study sites. The use of longer monitoring periods may elucidate in what extent airborne organic compounds remain active after leaf deposition.

3.3 Temporal-integration of leaf-deposited SVOCs: PCA analysis

The most discriminant components (PC1 and PC2) accounted for 15.2 and 9.2% of the total variance, respectively. The proportion of variation explained by the first two components is rather low, yet expected due to the large number and diversity of organic compounds detected (n = 911). Nonetheless, the score plot (Figure 2) indicates that PC1 mainly separates the leaf-deposited SVOCs obtained after 28 days from those obtained after one and seven days of exposure, whereas the latter appear more clustered together. The variance explained by PC2 points to a comparable interpretation for some cases only, with e.g. *G* (urban) site appearing in opposite directions depending whether the leaves were exposed for one or 28 days. Indeed, the exposure period revealed to be a significant factor for PC1 (linear model fit, P = 0.013) rather than for PC2 (P = 0.057). On the other hand, neither the study site nor the land use class showed to be a predictor of PC1 or PC2 (see P values in Table A.1). The geographic distances between study sites were also tested against the dissimilarities in SVOCs composition, but no significant spatial associations were found (Mantel test, P = 0.85). Therefore, the first exploratory study of SVOCs recovered from leaf washing solutions, hereby reported, strongly suggests a comparable trend for the time-cumulative collection of organic compounds among all study sites, while spatial variations appeared more difficult to detect. The hypotheses herein formulated should be carefully considered though, since they are based on exploratory data only and there are no experimental replicates to investigate the representativeness of the methodology, neither of the obtained data.

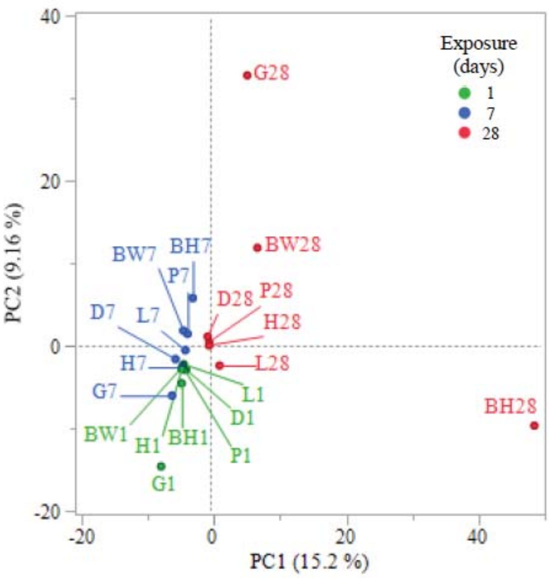

Figure 2 – PCA score plot of the 911 detected organic compounds in terms of their S/N ratio: projection in the PC1−PC2 plane of the coordinates of the analyzed samples. The analyzed conditions are labeled according to the study site (BH – Borgerhout, BW – Boudewijnsluis, D – Dessel, G – Groenenborgerlaan, H – Hoboken, L – Luchtbal, P – Park Spoor Noord) and exposure period (1, 7, 28 days).

3.4 Relation with pollutant concentrations at the co-located air monitoring stations

Even though the study sites were attributed to distinct land use classes, daily mean PM concentrations (both PM_{10} and $PM_{2.5}$) at the seven air monitoring stations exhibited similar temporal behavior over the entire exposure period (see Figure A.2), suggesting local PM sources had less influence compared to the urban/regional background. This between-sites temporal trend was verified by pairwise correlations ($P < 0.0001$) between all study sites with positive Kendall's correlation coefficients ($\tau = 0.56$ - 0.91 for PM_{10}, $\tau = 0.64$ – 0.95 for $PM_{2.5}$), while the land use showed no influence on PM_{10} or $PM_{2.5}$ ($P > 0.46$). The comparison of PM concentrations between study sites revealed no significant difference in $PM_{2.5}$ ($P = 0.070$), whereas this was significant for PM_{10} ($P = 0.014$), specifically between study sites *H* and *BW* (Tukey HSD, $P = 0.026$). Both these sites are attributed to the industrial land use class, although under the influence of distinct industrial activities, namely, metal-emitting (*H*) and petrochemical (*BW*). Variations in PM are known to peak at pollution hotspots, due to e.g. traffic-related and industrial sources, while comparable temporal patterns are often observed within the same region, under the influence of similar cross-boundary, national and eventually urban background concentrations, as well as meteorological conditions (Hofman et al., 2014a; Van Dingenen et al., 2004; Vercauteren et al., 2011). A consistent between-sites temporal trend was also observed for NO_2 (from six sites; $P < 0.0041$, $\tau = 0.41$ - 0.85) and O_3 (from two sites; $P < 0.0001$, $\tau = 0.76$), but not for SO_2 (measured at four sites). Daily SO_2 concentrations throughout the leaf campaign were negatively correlated between the *H* (industrial) and *D* (rural) sites ($P = 0.031$, $\tau = -0.29$), while positively correlated between the *H* (industrial) and *L* (mixed) sites ($P = 0.0005$, $\tau = 0.47$). *L* site is exposed to diverse polluting sources, including industry (ca. 2 km distant), while industrial SO_x emissions at *H* site are known to be considerable, almost 2.5 times larger than their NO_x emissions. Moreover, SO_2 concentrations were higher at *H* site in comparison to all other study sites ($P < 0.0001$). Comparable analysis revealed that O_3 concentrations were greater at site *D* (rural) than at *BH* (intense traffic), whereas NO_2 concentrations were significantly higher and lower at sites *BH* and *D*, respectively, in comparison to the other sites (*G*, *H*, *L*, *P*) ($P < 0.0001$). The high vehicle intensity at *BH* site explains the higher NO_2 concentrations compared to those at *D*, a rural, background site, while the prominent O_3 levels at the latter may be due to biogenic VOCs (BVOCs) emissions by the vegetation there present, a recognized catalyst for O_3 formation (Calfapietra et al., 2009).

No significant relations arose when testing the PC1 and PC2 scores against concentrations of PM_{10}, $PM_{2.5}$, O_3, NO_2, SO_2 at the co-located air monitoring stations on the day of leaf sampling (P values in Table A.1). Since the plants were exposed for a certain period of time, one could hypothesize that the detected SVOCs would be associated with the cumulative air concentrations rather than with the daily average on sampling day. However, no significant effects were found when considering the cumulative averaged concentrations since exposure (i.e. from day zero until leaf sampling day) nor from the two days prior to sampling. On the other hand, variations in the composition of leaf-deposited SVOCs for the considered study sites and exposure time showed to be significantly associated (Mantel tests, $P < 0.01$) with variations in PM_{10} and $PM_{2.5}$ concentrations on sampling day and averaged from two days prior to leaf sampling ($\tau = 0.16$ and $\tau = 0.19$ for PM_{10}, $\tau = 0.18$ and $\tau = 0.20$ for $PM_{2.5}$, respectively), but such relation was not present for cumulative PM. One could thus conclude that larger differences in PM_{10} and $PM_{2.5}$ concentrations on the day of sampling (or from two days before) lead to larger dissimilarities in the SVOCs composition. The causality of such relationship remains yet uncertain because the dissimilarity in SVOCs composition and the difference in PM concentrations correlate both significantly with the differences in exposure time (Mantel test). On the other hand, no influence ($P > 0.42$) was detected when testing the SVOCs dissimilarities against the variation of pollutants O_3, NO_2 and SO_2.

3.5 Conclusions

Air quality inspection through leaf monitoring is a valid, useful approach, often more cost- and time-effective than employing artificial active/passive samplers, enabling e.g. a denser sampling network. The collection of leaf-deposited compounds (as SVOCs and PM) through water washing, in alternative to aggressive solvent-based leaf extractions, is rather targeted to study compounds that easily get deposited/adsorbed to the leaf surface, as well as removed from it. Screening such leaf washing solutions may provide a rapid insight on distinct land uses or pollution sources, allowing for spatial and/or temporal monitoring studies.

Our results confirm the potential of GCxGC-TOFMS as an exploratory tool to investigate SVOCs recovered from the surface of ivy leaves. The diversity and composition of leaf-deposited SVOCs were in our study influenced by exposure time rather than by land use. In fact, SVOCs alteration and/or degradation after leaf deposition appeared more pertinent to their composition than local sources. Additional research on the topic should consider monitoring plants for longer exposure times, include sample replicates to increase data representativeness and a validation step with spiked compounds to gain more insight in terms of concentrations.

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