

Fine Particulate Abrasion Products from Leaf Surface of Urban Plants: Comparison between Pittsburgh and Los Angeles

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ABSTRACT

Whenever ambient fine particulate matter is collected and analyzed for organic constituents, the contributions of fine particulate waxy leaf surface matter can be easily identified by the peculiar biogenic preference. The preference is for higher molecular weight odd vs. even carbon number n-alkanes and for even vs. odd n-alkenoic acids.

In order to determine the contributions of fine particulate leaf surface wax abrasions to the ambient PM_{2.5} levels, suitable source profiles have to be available. Up to now, only one source profile has been available for leaf samples collected in Los Angeles (Rogge et al., ES&T, 27, 2700-2711, 1993; Hildemann et al., ES&T, 25, 744-759, 1991; Hildemann et al., JGR, 101, 19,541-19,549). Today, the Los Angeles organic source profiles for leaf surface abrasions are widely used throughout the USA for source apportionment studies, despite the different distribution of plants and trees from location to location.

Here, an additional source profile for organic constituents associated with fine particulate leaf surface abrasion products has been generated for Pittsburgh, PA. Green leaves from 11 common tree species that are characteristic for the Pittsburgh area were harvested during September of 2003 and composited according to the tree distribution for that area. To simulate a windblown generation process that dislodges waxy leaf surface protrusions, the leaf composite was placed in a clean Teflon bag and mechanically agitated while passing purified air through the bag, similar to the procedure used for the Los Angeles leaf samples. The fine waxy protrusions ($d_p \leq 2.5 \mu\text{m}$) shed from the leaf surfaces were extracted and analyzed using gas chromatography/mass spectrometry. Individual organic compounds were identified including: n-alkanes, iso- and anteiso-alkanes, n-alkenoic acids, n-alkenoic acids, alkanals, n-alkanones, steroids, pentacyclic triterpenoids, phenolic type compounds, and others. Trace amounts of PAH were identified and quantified as well.

PROBLEM AND APPROACH

Why generate a source profile for PM_{2.5} leaf surface abrasion products?

- Due to wind-induced mechanical shear and the rubbing motion of leaves against each other, an unspecified amount of fine particulate epicuticular wax protrusions and leaf deposits are released to the atmosphere that have been identified in urban and rural ambient PM_{2.5} samples. In order to determine the contributions of these waxy epicuticular fine particles to the atmospheric fine particle burden, source profiles have to be available for the sites of interest.

Approach:

- Similar to the Los Angeles study, leaves were collected from the major 11 tree types common to the Pittsburgh area. This tree distribution is generally representative of forests that are described as a "Mixed Oak Forest" or "Appalachian Oak Forest". The leaves were collected from the Schenley Park, a park with 500 acres that is situated in Pittsburgh. The park is influenced by human activities, including picnic areas equipped with barbecue places.
- According to the distribution of tree species, an appropriate number of green leaves from each species were composited and placed in a Teflon bag. While the leaves were agitated, purified laboratory air was blown into the bag through a HEPA filter. Simultaneously, particle-laden air was withdrawn from the bag and collected on quartz fiber filters using a PM_{2.5} sampling system.
- The filter samples were subsequently extracted with methylene chloride. Prior to extraction, known amounts of a suite consisting of 7 perfluorinated n-alkanes were spiked onto the filter samples. The amount added was based on the organic carbon (OC) content of the samples as determined by OC/EC analysis.
- The fine particulate leaf surface abrasion products were extracted successively four times by mild ultrasonic agitation with methylene chloride. The total sample extract was combined and reduced to about 100 μL using rotary evaporation followed by gentle high-purity N₂-stream evaporation.
- Next, the sample extracts were treated with diazomethane, in order to convert carboxylic acids to their methyl ester analogues. Sample extracts were then analyzed using an Agilent 6890 Gas Chromatography equipped with a 30 m long DB-5MS column, coupled to an Agilent 5973 Mass Selective Detector.



Pittsburgh Vegetation Sample Composite	Fraction of Mass in Composite in %
Simulacraea	7.2
White Ash	6.3
Ohio Buckeye	1.0
Wild Red Cherry	2.2
Black Oak	13.4
American Elm	5.0
Scarlet Hawthorne	4.0
Norway Maple	51.4
Common Locust	5.4
Pink Oak	1.5
Slippery Elm	2.5

Los Angeles Vegetation Sample Composite	Fraction of Mass in Composite in %
BROAD LEAF TREES	
Ribbon Gum	2.10
Ash	1.36
Calif Live Oak	1.00
Elm	0.25
Maple	0.20
Calif Sycamore	0.22
Peruvian Pepper	0.21
Jacaranda	0.15
Victorian Box	0.91
Robinia pseudoacacia	0.97
Crape Myrtle	0.66
Avocado	0.26
Cinnamomum camphora	0.09
Magnolia grandiflora	0.06
Brazilian pepper	0.018
Olive	0.16
Sallee	0.01
Silver dollar gum	0.10
Citrus (orange)	0.11

SHRUBS		
Calif Sage Brush	Artemisia californica	0.065
Golden Wattle	Acaia longifolia	0.51
Juniper	Juniperus sp.	2.17
Glossy Privet	Ligustrum lucidum	0.26
Botanibush	Callitemon sp.	0.41
Chinese Juniper	Juniperus chinensis	0.98
Camellia	Camellia sp.	0.75
Oleander	Nerium oleander	0.14
Hibiscus	Hibiscus sp.	0.26
Rosa sp.	Rosa sp.	0.11
Shiny Xylosma	Xylosma congestum	0.16
Coyote Bush	Baccharis pilularis	0.25
Yucca	Yucca sp.	0.32
Yucca	Heteromeles arbutifolia	0.32
Cape homysuckle	Tecomaria capensis	0.028
Colemania	Colemania sp.	0.11
Heavenly bamboo	Nandina domestica	0.053
India Hawthorn	Raphiolepis pilularis	0.075
Holly	Ilex sp.	0.056
Podocarpus	Podocarpus sp.	0.047
Yucca	Yucca sp.	0.31

CONIFERS		
Monterey Pine	Pinus radiata	1.29
Other Pine	Pinus sp.	0.45
Italian Cypress	Cupressus sempervirens	2.87

PALMS		
Cocco Palm	Archontophoenix nortoniaefolium	0.58
Fox Palm	Washingtonia sp.	0.26
Canary Is. Palm	Phoenix canariensis	0.33

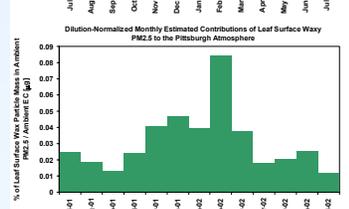
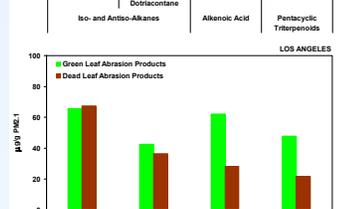
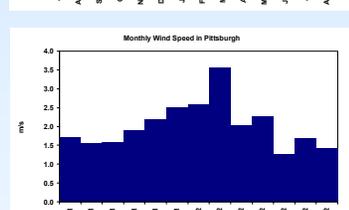
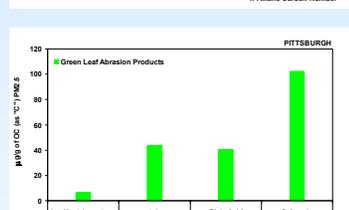
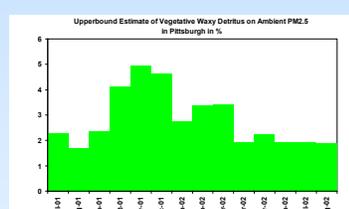
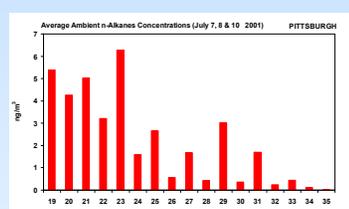
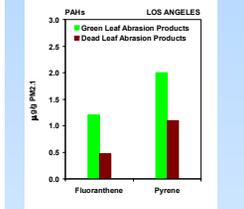
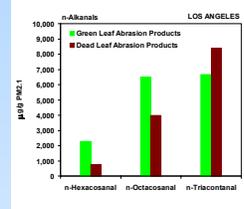
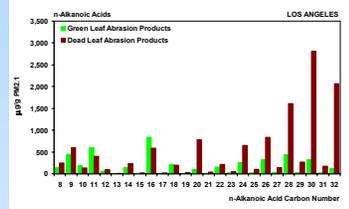
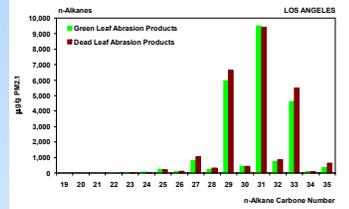
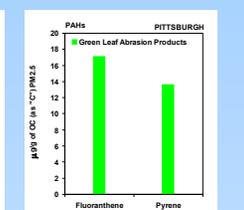
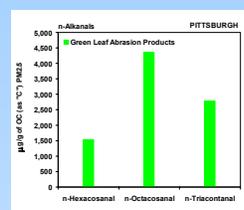
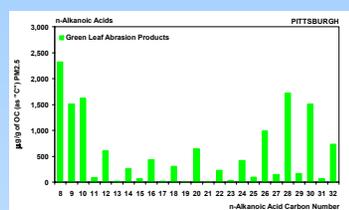
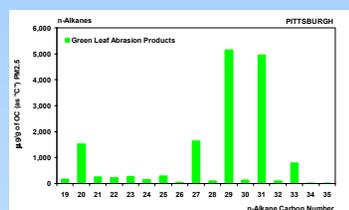
GRASS		
Mixed grasses	(Various unidentified)	17.42
Dichondra repens	Dichondra repens	0.97

GROUND COVER		
Ivy	Hedera sp.	2.55
African Daisy	Osteospermum fruticosum	1.95
Ice Plant	Lamprunus speciosulus	1.92

NATURAL VEGETATION		
Black Sage	Salvia sp.	6.25
Buckthorn	Rhamnus sp.	0.44
Buckwheat	Eriogonum sp.	1.40
Calif. sage brush	Artemisia californica	0.36
Ceanothus	Ceanothus sp.	14.27
Chamise	Adenostoma sp.	2.86
Manzanita	Arctostaphylos sp.	10.84
Scrub oak	Quercus sp.	6.53
Sugar bush	Rhus sp.	2.08
Grass	Gramineae	18.85

From: Hildemann, L. M.; Markowski, G. R.; Cass, G. R. 1991. "Chemical Composition of Emissions from Urban Sources of Fine Organic Aerosol." Environmental Science Technology, 25, 744-759.

RESULTS



CONCLUSIONS

For the Pittsburgh leaf surface abrasion sample, the EC and OC have been measured; however, PM_{2.5} mass is not available. Therefore, for the purpose of comparing the Pittsburgh profile with the Los Angeles profiles it was assumed that for the Pittsburgh sample 80% of the PM_{2.5} mass was OC.

Higher molecular n-alkanes associated with leaf waxes show a pronounced preference for odd carbon numbered n-alkanes at both locations. Waxy n-alkanes concentration levels for the Pittsburgh leaf abrasion sample is somewhat lower than found for Los Angeles, possibly a result of the different plant distribution as well as differences in climate between the two locations.

n-Alkanoic acids in leaf surface waxy protrusions show a strong preference for even carbon numbered n-alkanoic acids for carbon number greater than C14. Comparing the source profiles for leaf surface abrasion products from green leaves, it can be seen that the concentrations for higher molecular weight (≥C₂₄) even carbon numbered n-alkanoic acids is about 2-3 times higher at Pittsburgh than measured in Los Angeles. A more than 4-fold increase in the mass concentration of higher molecular weight n-alkanoic acids (≥C₂₄) is observed in dead leaf abrasion products. Possible explanations include oxidation of n-alkanoic acids to form n-alkanoic acids in the dead leaf material and/or the effect of environmental growth conditions (e.g., temperature) or leaf age on wax composition.

In the Pittsburgh fine particulate leaf surface sample, no n-alkanoic acids were identified. Consequently, no comparison for these compound class is possible between these two locations. Also, only the major n-alkanoic acids could be identified in the Pittsburgh sample and these show somewhat lower concentrations than determined for Los Angeles.

Because ambient particulate matter is deposited onto surfaces, including leaf surfaces, it is not surprising to find as well PAHs. Fluoranthene and pyrene show about 10 times higher concentrations in the leaf surface abrasion products in the Pittsburgh sample when compared to Los Angeles samples. This is not surprising, considering the substantially higher ambient PAHs concentrations in Pittsburgh than typically found in Los Angeles.

Doing "back of the envelop" estimations, no more than 3-4% of the ambient PM_{2.5} concentrations are derived from leaf surface wax particles. Normalizing the contributions of leaf surface wax particles to the ambient PM_{2.5} concentrations by a "conservative" compound (e.g., EC) that is released more or less with the same emission strength throughout the year, allows the removal of the influence of seasonal changes associated with the height of the inversion base. To a first approximation, any seasonal variations that remains after normalization with EC can be attributed to variations in the emissions of particle-borne leaf surface abrasion products. Doing so, it can be seen that most emissions of leaf surface abrasion products do occur during Fall-Spring.