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**Water-soluble  
atmospheric HULIS in  
urban environments**

C. Baduel et al.

# Water-soluble atmospheric HULIS in urban environments

**C. Baduel, D. Voisin, and J.-L. Jaffrezo**

Université Joseph Fourier – Grenoble 1/CNRS – INSU, Laboratoire de Glaciologie et Géophysique de l'Environnement, rue Molière, 38402 Saint-Martin-d'Hères, France

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Correspondence to: D. Voisin (didier.voisin@ujf-grenoble.fr)

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Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



## Abstract

Major contributors to the organic aerosol include water-soluble macromolecular compounds (e.g. HULIS<sub>WS</sub>). The nature and sources of HULIS<sub>WS</sub> are still largely unknown. This work is based on a monitoring in six different French cities performed during summer and winter seasons. HULIS<sub>WS</sub> analysis was performed with a selective method of extraction complemented by carbon quantification. UV spectroscopy was also applied for their chemical characterisation. Strong differences in the optical properties and therefore in the chemical structure (i.e. the aromaticity) between HULIS<sub>WS</sub> from samples of summer- and wintertime are found. These differences highlight different processes responsible for emissions and formation of HULIS<sub>WS</sub> according to the season. Specific absorbance can also be considered as a rapid and useful indicator of the origin of HULIS<sub>WS</sub> in urban environment.

## 1 Introduction

The composition of the organic fraction of atmospheric aerosols and the respective contributions of primary and secondary sources are still poorly known, in part due to the considerable number of chemical species present in the particles. During the last years it was shown that HUmic LIke Substances (HULIS, i.e. polyacidic macromolecular species), are important contributors to the mass of the organic aerosol in rural, urban, marine, and biomass burning aerosol (Salma et al., 2007). The water soluble fraction of HULIS (HULIS<sub>WS</sub>) most likely influences the hygroscopicity and the CCN ability of particles (Dinar et al., 2006; Salma et al., 2008; Hatch et al., 2008) as well as their optical properties (Dinar et al., 2008). Currently, atmospheric HULIS research is hindered by the lack of a unified method for the analysis of these compounds and by a lack of knowledge on their sources (Graber and Rudich, 2006), and references therein). Recently, Feczko et al. (2007) showed a seasonal cycle of HULIS concentrations for six background sites, with one maximum in summer and another one in

### Water-soluble atmospheric HULIS in urban environments

C. Baduel et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



winter. These variations have been seen as due to changes in either the sources of HULIS, or their formation processes, assuming that HULIS consist in a mixture of primary emissions and secondary products of various origins. In this paper, we investigate the temporal and structural variation of the HULIS<sub>WS</sub> fraction collected in urban environments.

## 2 Experimental section

### 2.1 Sampling

Aerosol samples were collected in the urban background of 6 large French cities: Grenoble, Strasbourg, Lille, Paris, Toulouse, and Marseilles. Samples were collected on quartz fiber filters (150 mm diameter, Whatman, Q-MA) using DA-80 high volume samplers (DIGITEL), operating at  $30 \text{ m}^3 \text{ h}^{-1}$ . The filters were prepared before collection by firing them during 2 h at  $600^\circ\text{C}$ . Sampling duration in Marseilles was based on a day/night pattern, with 12 h sampling for a total period of 14 days during summer 2008. The sampling for all other locations took place daily once or twice a week, for periods of several months in summer 2008 and/or in winter 2008. Sampling periods and numbers of samples are reported in Table 1. More details about these different campaigns can be found elsewhere (El Haddad et al., 2009; Pissot et al., 2009). Additional samples were collected in the small town of Chamonix, located in a valley of the French Alps (Aymoz et al., 2007). The sampling took place for a period of 10 days in winter 2007 (10 to 19 December 2007) in a suburban location. Sampling duration was based on a day/night pattern, with 12 h sampling.  $\text{PM}_{10}$  samples were collected on quartz fiber filters (Whatman<sup>®</sup>, 150 mm diameter) with a high-volume sampler (Tisch Andersen) at a flow rate of  $30 \text{ m}^3 \text{ h}^{-1}$ . More details about sampling can be found elsewhere (Baduel et al., 2009). Finally, some samples are coming from a tunnel study conducted in Marseilles in spring 2008 (El Haddad et al., 2009). They were also collected with a similar protocol, except for a much shorter sampling time. After sampling, all filters

## Water-soluble atmospheric HULIS in urban environments

C. Baduel et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



were wrapped in aluminium foils, sealed in polyethylene bags and stored frozen until further analysis.

## 2.2 Analysis

These atmospheric samples are analyzed for EC/OC (Elemental and Organic Carbon), WSOC (Water Soluble Organic Carbon), and HULIS<sub>WS</sub> concentrations. EC/OC concentrations are determined by Thermo-Optical Transmission (TOT) method on a Sunset Lab analyzer (Aymoz et al., 2007). We are using the newly developed EUSAAR2 temperature program (Cavalli and Putaud, 2009). It includes temperature steps up from 200 to 650°C for the analysis of OC in 100% He, and up from 500 to 700°C for the analysis of EC in 98% He+2% O<sub>2</sub>. Automatic split time was always used for the distinction between EC and pyrolyzed OC. We analyzed fractions of 1.5 cm<sup>2</sup> of the filters, without any preparation.

For WSOC determination, 17–20 cm<sup>2</sup> of filter are extracted during 30 min in 12 mL of organic free water (Elgastat<sup>®</sup>). The surfaces extracted are adapted according to the OC concentrations measured in each sample. The extracts are filtered with Acrodisc filters (Pall Gellman<sup>®</sup>, 0.22 μm porosity) to remove any particles in suspension. WSOC is quantified with a DOC analyser (Shimadzu TOC-VCPH/CPN) by catalytic burning at 680°C in oxygen followed by non dispersive infrared detection of the evolved CO<sub>2</sub>.

The water soluble HULIS fraction is analyzed according to a protocol described in detail elsewhere (Baduel et al., 2009). Briefly, the water soluble fractions obtained from aerosol samples are passed through a weak anion exchange resin (GE Healthcare<sup>®</sup>, HiTrap<sup>™</sup> DEAE FF, 0.7 cm ID×2.5 cm length) without any pre-treatment. After this concentration step, the organic matter adsorbed is washed with 12 mL of a solution of NaOH 0.04 M (J.T.Baker<sup>®</sup>, pro analysis) to remove neutral components, hydrophobic bases, inorganic anion, mono- and di-acids initially retained in the resin. Finally, HULIS<sub>WS</sub> are quickly eluted in a single broad peak using 4 mL of a high ionic strength

### Water-soluble atmospheric HULIS in urban environments

C. Baduel et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



solution of NaCl 1 M (Normapur<sup>®</sup>). All flow rates are set at 1.0 mL min<sup>-1</sup>. In this case, HULIS<sub>WS</sub> are operational defined as polyacidic compounds. UV-Vis absorption spectra are measured on-line after the extraction system, using a diode array detector (Dionex UV-VIS 340U), and recorded in the range 220–550 nm. The HULIS<sub>WS</sub> fraction is subsequently collected manually and the carbon content is analyzed with the same DOC analyser used for WSOC determination.

### 3 Results and discussion

#### 3.1 Atmospheric concentrations

The average concentrations and contributions of the HULIS<sub>WS</sub> fractions for all campaigns are presented in Table 1. The concurrent measurements of concentrations for OC, WSOC, and HULIS<sub>WS</sub> allow several observations. First, the concentrations of HULIS<sub>WS</sub> vary from 0.51 in the summer to 2.11 µg Cm<sup>-3</sup> in the winter. A small tendency for a winter maximum can be observed. This is in contradiction with previous results (Krivácsy et al., 2008), indicating a strong winter maximum for urban polluted background. This difference can probably be related to our selective extraction protocol. Indeed, we will show that our samples are strongly impacted by biomass burning emissions, and functionalized aromatic compounds (like phenol, vanillin, syringaldehyde, etc . . . ) are consistently emitted by such sources (Graham et al., 2002). These compounds are associated with the HULIS fraction for the protocol used by Krivácsy et al. (2008), according to Limbeck et al. (2005) while they are excluded from it in our protocol (Baduel et al., 2009).

Second, the contribution of HULIS<sub>WS</sub> to WSOC as measured in our study is between 28–43% and the contribution to OC is in the range 14–22%. The HULIS<sub>WS</sub> contributions in our study are comparable to data obtained with a comparable method for polluted rural background: 24–44% of WSOC for a yearly study (Decesari et al., 2001).

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Finally, rather large concentrations of HULIS<sub>WS</sub> are measured in vehicle emissions as compared to HULIS<sub>WS</sub> concentrations found in urban background in summer. However, in the former case HULIS<sub>WS</sub> only represent a relatively small fraction of OC due to the important hydrophobic character of freshly emitted organic aerosol in vehicle exhaust (El Haddad et al., 2009).

### 3.2 Chemical characterisation

It is largely demonstrated that HULIS present light absorption in the UV-Vis range (Graber and Rudich, 2006). The absorption at wavelengths ranging from 250 to 300 nm is mainly attributed to  $\pi-\pi^*$  electron transitions in the double bonds of aromatic compounds. In research on aquatic humic substances, several studies indicated large correlations between absorbance and carbon concentrations measured with DOC analyzers, for various wavelengths, i.e. 250, 254, 285, 330, and 350 nm (Hautala et al., 2000). Absorbance of such samples increases with its pH, and also with total carbon content, its aromaticity, and its average molecular weight (Chen et al., 1977).

Since HULIS consist in polyfunctional compounds made up of a heterogeneous mixture of aliphatic and aromatic structures (Graber and Rudich, 2006) and generally include relatively highly aromatic compounds, we choose to present data for the absorbance at 250 nm, because most of the aromatic structures show strong absorption at this wavelength. Table 1 presents correlations between HULIS<sub>WS</sub> concentrations and its absorbance at 250 nm for the different sites and seasons.

First, one can see that for the overall sample set obtained in Grenoble in 2008 (the only one covering all seasons), we can observe three different trends, corresponding to samples collected in summer, winter, and mid seasons, respectively. High (resp. low) specific absorbance during the cold (resp. warm) season lead to high (resp. low) slope for the regressions between concentrations and absorbance, with results from mid seasons in-between. Correlations for the regression lines are excellent and values of the average specific absorbance for each season are statistically different, indicating a consistent pattern over each of the data sets. Further, the intercepts are low in each

## Water-soluble atmospheric HULIS in urban environments

C. Baduel et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



case, an indication that our extraction protocol is efficient in getting rid of any inorganic species absorbing at 250 nm. Second, the table indicates that all other sample sets follow a similar pattern, with large specific absorbance in the cold season and a much lower one in summer, irrespective of the sampling locations. For each site and each season, regressions between absorbance and concentrations also present excellent correlation coefficients.

### 3.3 Characteristics of the combined data sets

In a second step, samples from the different sites are gathered according to the sampling season and the associated regression lines are plotted in Fig. 1. It shows that the correlations between the concentrations of HULIS<sub>WS</sub> and its absorbance at 250 nm are strongly different between the summer ( $n=65$ ) and winter ( $n=73$ ) sample sets. This agrees well with different chemical structures for winter and summertime HULIS<sub>WS</sub>, which can be related to seasonal differences in emissions and/or formation processes. Moreover, the excellent correlation for each regression shows the stability of the bulk structure of the HULIS<sub>WS</sub> extracted during these two different periods, with a very low dependency on the specific site.

#### 3.3.1 Winter

HULIS<sub>WS</sub> collected in winter present a strong absorbance at the wavelength of 250 nm, which can be mainly attributed to an important contribution of aromatic structures. As mentioned above, it is known that biomass combustion processes release aromatic species at high concentration into the atmosphere (Graham et al., 2002). It is proposed that such combustions represent the most probable source of HULIS<sub>WS</sub> in urban areas during the burning season (Krivácsy et al., 2008). This is further supported by the correlations between HULIS and biomass burning tracers such as levoglucosan, dehydroabietic acid, and fine potassium (Feczko et al., 2007; Krivácsy et al., 2008; Mayol-Bracero et al., 2002). These results are also in good agreement with recent

## Water-soluble atmospheric HULIS in urban environments

C. Baduel et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



chemical characterisation studies of WSOC from biomass burning source (Duarte et al., 2008; Decesari et al., 2007). A primary mode of HULIS formation could derive from the incomplete breakdown of polymeric carbohydrates and lignin which can be further modified in the process of combustion. HULIS formation can also be secondary in nature, resulting from the transformation of pyrogenic semi-volatile organic compounds through condensation reactions with other molecules (Mayol-Bracero et al., 2002). Hoffer et al. (2004) also showed that HULIS may be produced in cloud droplets from aromatic acid precursors which may originate from biomass burning. Finally, Decesari et al. (2002) proposed that HULIS can derive from the reaction of soot particles with atmospheric oxidants. In this case, reactions with ozone can lead to the degradation of aromatic structures and to the formation of carbonyls and carboxyls functional groups (Bloss et al., 2005).

In our case, a strong correlation between  $HULIS_{WS}$  and biomass burning tracers for each sampling campaign in urban background during winter is demonstrated (Pissot et al., 2009). Wood combustion is therefore probably the main source of  $HULIS_{WS}$  in the large French cities during winter. Yet,  $HULIS_{WS}$  collected in Chamonix present a stronger absorbance than those collected in winter in other cities (Table 1 and Fig. 1) while we know that a very large fraction of the PM at this site is due to local emissions of wood combustion from domestic heating (Marchand et al., 2004). Therefore, the absorbance of the  $HULIS_{WS}$  in these last samples can probably be regarded as representative of  $HULIS_{WS}$  freshly formed during biomass burning processes. The difference in specific absorbance between the large cities and the Chamonix samples possibly indicates a degradation of aromatic rings during aging of aerosol in the atmosphere. Further investigations on this point are in progress, with direct measurements of  $HULIS_{WS}$  fractions and characteristics from samples collected at the emission from different sources of biomass burning. Another possible explanation to this lower specific absorbance in the cities compared to Chamonix samples, would be mixing with another source of less absorptive  $HULIS_{WS}$ . Automobile traffic, as represented by our tunnel samples, could be such a source. Considering, in a very crude approximation,

---

**Water-soluble  
atmospheric HULIS in  
urban environments**C. Baduel et al.

---

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

that our winter HULIS<sub>WS</sub> result from mixing of these sole two sources, the observed specific absorbance would be explained by a contribution of 47% from biomass burning, which is roughly in line with source apportionment based on levoglucosan concentrations on the same samples (Pissot et al., 2009).

### 3.3.2 Summer

Summer HULIS<sub>WS</sub> present a lower absorbance, an indication of a more pronounced aliphatic character. Such structures may belong to secondary products from some biogenic or anthropogenic sources. Decesari et al. (2007) suggested secondary atmospheric oxidation processes as possible sources for atmospheric WSOC in an urban area in summer. This last study also showed that the composition of biogenic and anthropogenic secondary organic aerosol (SOA) are characterized by a high content of aliphatic structures (high H-C content and H-C-O) and a systematic low aromatic content. Numerous investigations have confirmed the existence of polymeric/oligomeric compounds with molecular masses up to 1600 Da in various SOA formed from photooxidation of both anthropogenic (Gross et al., 2006; Wyche et al., 2009) and biogenic (Surratt et al., 2006; Tolocka et al., 2004) precursors in simulation chamber studies. Such polymeric products present spectral properties similar to HULIS in atmospheric aerosols (Limbeck et al., 2003), despite the fact that the majority of HULIS compounds seem to be in the range of 400–700 Da (Graber and Rudich, 2006). During warmer periods in urban site, maximum molecular weight of the HULIS determined with SEC-UV had shown positive correlations with temperature and ozone. These results suggest photochemical processes as a source of secondary HULIS (Samburova et al., 2005). Finally, Zhang et al. (2007) identified a highly oxygenated fraction in organic aerosol that presents a mass spectrum resembling that of fulvic acids, (e.g. a reference compound for HULIS) with a larger abundance at sites influenced by urban transport. The synthesis is that, in urban environments, HULIS can both be secondarily formed by chemical reactions from various precursors and directly emitted into the atmosphere by fossil fuel combustion. Our data show that ambient HULIS<sub>WS</sub> in summer exhibit a lower

## Water-soluble atmospheric HULIS in urban environments

C. Baduel et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



specific absorbance than  $HULIS_{WS}$  representative of the primary automobile emission source. This could be viewed as a mixture process between this primary source and secondarily produced  $HULIS_{WS}$  exhibiting a much lower specific absorbance.

However, recent studies with H-NMR have shown that concentrations of carboxylic and carbonyl functional groups and their contribution to WSOC increase with photochemical activity and are associated with a decrease in the density of aromatic and hydroxylic groups (Moretti et al., 2008). It confirms that prolonged aging of SOA leads to the formation of carboxylic functional groups in agreement with results of AMS measurements at different sites (Lanz et al., 2007). These evolutions associated with aging could explain in part the differences observed in our data between the measurement in the tunnel and those in the urban backgrounds.  $HULIS_{WS}$  from primary vehicular emissions, with an already low specific absorbance of  $29.3 \pm 3.5$  (Table 1) indicative of compounds with a rather aliphatic character, would lead to even lower absorbance during aging. In order to choose between those two hypotheses (mixing and aging), it is now necessary to obtain spectral data on secondarily produced  $HULIS_{WS}$ .

### 3.3.3 SRFA and use of specific absorbance

Suwannee River Fulvic Acid (SRFA) (IHSS, 1S101F) is mainly used in the literature as a model compound for atmospheric  $HULIS_{WS}$  for different kind of experiments (Baduel et al., 2009). However, it is hypothesized that  $HULIS_{WS}$  show structural differences with aquatic humic substances, like a higher aliphatic structure and a lower degree of oxidation (Graber and Rudich, 2006). A data set for SRFA was obtained in our study for measurements on the same standard solution, for a range of carbon masses between 0 and 20  $\mu\text{g}$ . Table 1 indicates that this standard compound presents a specific absorbance at 250 nm close to that of the samples collected in urban areas in winter, with a slightly lower value compared to that obtained for the data set from the Alpine valley in Chamonix. Conversely, characteristics of  $HULIS_{WS}$  collected in summer may largely differ from that of SRFA, with a much lower absorbance at 250 nm for the former. Therefore, it is not appropriate to consider SRFA as a representative standard for the

## Water-soluble atmospheric HULIS in urban environments

C. Baduel et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



whole HULIS<sub>WS</sub> fraction. Absolute calibration of UV absorbance with SRFA can not be used for quantification of HULIS<sub>WS</sub> because it can overestimate the carbon content of HULIS by a factor of 3.

However, UV absorption could be a useful and rapid indicator of the origin of HULIS<sub>WS</sub> in atmospheric samples. Figure 2 presents specific absorbance in our samples as a function of the time of year. Average values of 22.6±4.5 in summer and 42.3±6.0 in winter were observed. Relative standard deviation represent about 15–20% in summer and 10–15% in winter, much lower than the relative seasonal variation. We can conclude that this measurement is useful to give a good idea of the formation processes of the HULIS<sub>WS</sub> fractions.

## 4 Conclusions

A monitoring in six different French cities has been realised during summer and winter seasons. Water-soluble HULIS comprises about 23–43% of WSOC and 13–23% of OC in different urban environments. The HULIS contribution is significant indicating the global importance of HULIS in controlling the mass concentration of organic aerosol. Specific absorbance at 250 nm was used to investigate structural differences in HULIS<sub>WS</sub> as a function of sampling site and season. Specific absorbance does not significantly change from one city to another for a given time period, but depends strongly on the season. Summer HULIS<sub>WS</sub> exhibit a lower specific absorbance, characteristic of more aliphatic/less aromatic structures. Those seasonal differences are more significant than any intra-seasonal or geographic variability, which points to formation processes or sources largely independent of the local emissions. Summer specific absorbance of HULIS<sub>WS</sub> is lower than the specific absorbance observed for traffic emitted HULIS<sub>WS</sub>, which could be explained by mixing with secondarily produced HULIS<sub>WS</sub> that would have even lower specific absorbance. Winter specific absorbance of HULIS<sub>WS</sub> is intermediate between the specific absorbance observed for biomass burning HULIS<sub>WS</sub> and traffic HULIS<sub>WS</sub>, which can be explained by a mixing process

### Water-soluble atmospheric HULIS in urban environments

C. Baduel et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



between those 2 sources. However, in both seasons, ageing of primary combustion emissions would lead to a breakdown of aromatic structures and thus lower the specific absorbance. This would also fit with our observations. In order to resolve those alternatives, specific experiments on ageing of biomass burning emissions and on specific absorbance of secondarily produced HULIS<sub>WS</sub> are necessary. Our investigations have been specifically targeted at the specific absorbance at 250 nm, because this is knowingly related to aromatic structures. Similar data at other wavelength could provide additional information on this ageing versus mixing alternative.

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ACPD

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## Water-soluble atmospheric HULIS in urban environments

C. Baduel et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



---

**Water-soluble  
atmospheric HULIS in  
urban environments**C. Baduel et al.

---

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Baduel, C., Voisin, D., and Jaffrezo, J. L.: Comparison of analytical methods for Humic Like Substances (HULIS) measurements in atmospheric particles, *Atmos. Chem. Phys.*, 9, 5949–5962, 2009,

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**Water-soluble  
atmospheric HULIS in  
urban environments**

C. Baduel et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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**Water-soluble  
atmospheric HULIS in  
urban environments**C. Baduel et al.

---

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

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**Water-soluble  
atmospheric HULIS in  
urban environments**

C. Baduel et al.

---

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



## Water-soluble atmospheric HULIS in urban environments

C. Baduel et al.

**Table 1.** Variations of mean concentration of Water Soluble HULIS (in  $\mu\text{g C m}^{-3}$ ) with standard deviation and its contribution to WSOC and OC aerosol fractions for each sample set. Correlations between TOC ( $x$ ,  $\mu\text{g C}$ ) and absorbance data at 250 nm ( $y$ , AU) expressed in an arbitrary unit for different sample sets from urban environments in summertime and/or in wintertime. The specific absorbance is the average value of the whole sample set for each described site. Uncertainties include standard deviation of the sample set.

Season	Location and sampling month	Number of samples	HULIS <sub>WS</sub> ( $\mu\text{g C m}^{-3}$ )	HULIS <sub>WS</sub> /OC (%)	Contribution WSOC (%)	Regression ( $x=\mu\text{g C m}^{-3}$ ; $y=\text{AU m}^{-3}$ )	Correlation factor ( $R^2$ )	Specific absorbance (AU/ $\mu\text{g C}$ )
Urban environment during cold season	Paris 08 Jan–Mar	16	1.08±0.86	14.6±3.2	34.1±9.0	$y=36.4x+3.2$	0.99	39.8±4.0
	Lille 08 Jan–Mar	10	0.85±0.41	16.0±5.1	40.3±10.0	$y=41.5x-0.1$	0.92	41.5±6.4
	Strasbourg 08 Jan–Mar	16	1.17±0.80	22.7±6.8	38.3±5.4	$y=41.3x-0.7$	0.98	39.5±6.1
	Grenoble 08 Jan–Mar	9	2.11±1.06	16.4±6.1	39.5±7.6	$y=46.7x-5.4$	0.98	43.2±4.2
	Grenoble 08 Mar, Apr, Oct	22	0.54±0.25	16.1±4.0	33.3±7.8	$y=37.0x+1.6$	0.89	46.0±5.9
Biomass burning background	Chamonix 07 Dec	16	1.47±0.95	12.7±1.8	23.4±3.1	$y=58.1x+0.8$	0.98	58.9±6.5
Primary vehicle emission	Tunnel in Marseilles	4	2.15±1.30	2–5	18–25	$y=26.9x+3.9$	0.96	29.3±3.5
Urban environment during summer	Marseilles 08 Jul	28	0.68±0.38	14.2±4.1	28.4±6.8	$y=19.6x+1.6$	0.90	20.6±4.1
	Toulouse 08 Jun–Aug	18	0.51±0.30	17.3±5.0	42.7±10.8	$y=15.3x+3.5$	0.69	22.6±5.8
	Grenoble 08 May–Aug	19	0.62±0.28	17.2±5.1	36.3±7.3	$y=17.1x+2.0$	0.82	21.8±3.0
Mid season	Grenoble 08 Mid-Apr and Sep	11	0.55±0.32	16.7±5.6	36.9±8.7	$y=32.1x-3.0$	0.99	30.6±2.7
Standard	SRFA (IHSS)	10					0.98	52.1±3.0

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

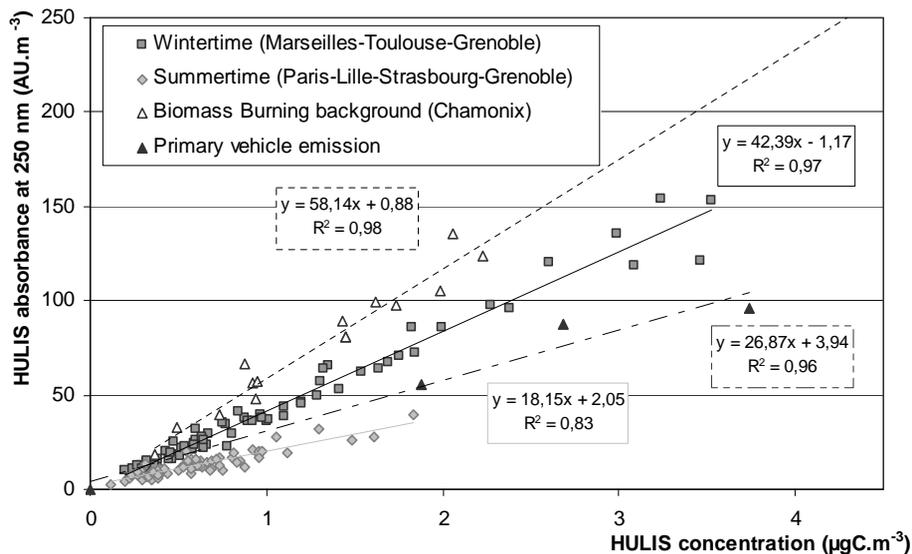
Printer-friendly Version

Interactive Discussion



Water-soluble  
atmospheric HULIS in  
urban environments

C. Baduel et al.

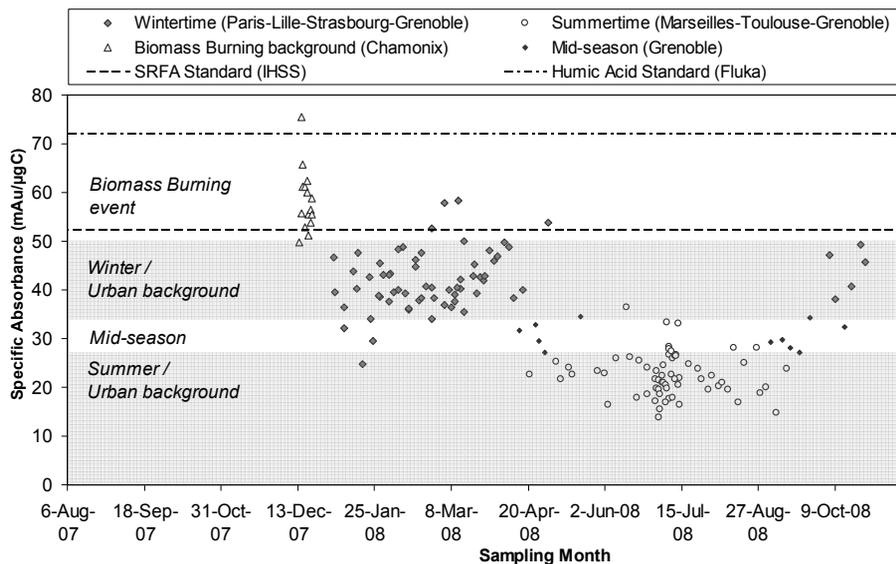


**Fig. 1.** Correlations between HULIS carbon concentration ( $\mu\text{gC}$ ) and UV HULIS absorbance datas at 250 nm (Arbitrary Unit per cube meter). Atmospheric HULIS data coming from different French cities are gathered by seasons. HULIS coming from Chamonix (biomass burning background) are not mix with other winter sample set.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

## Water-soluble atmospheric HULIS in urban environments

C. Baduel et al.



**Fig. 2.** Specific absorbance at 250 nm of HULIS from atmospheric aerosol samples depending on sampling season and environment.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)