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# Comparison of analytical methods for HULIS measurements in atmospheric particles

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

Laboratoire de Glaciologie et Géophysique de l'Environnement (UMR 5183), Université Joseph Fourier-CNRS, Rue Molière, BP 96, 38 402 St Martin d'Hères, France

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

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## Abstract

Humic-Like Substances (HULIS) are a major contributor to the organic carbon in atmospheric aerosol. It would be necessary to standardise an analytical method that could be easily and routinely used for HULIS measurements. We present one of the first comparisons of two of the main methods in use to extract HULIS, using i) a weak anion exchanger (DEAE) and ii) the combination of two separation steps, one according to polarity (on $C_{18}$) and the second according to acidity (with a strong anion exchanger SAX). The quantification is performed with a DOC analyzer, complemented by an investigation of the chemical structure of the extracted fractions by UV-Visible spectroscopy. The analytical performances of each method are determined and compared for humic substances standards. These methods are further applied to determine the water extractable HULIS ($HULIS_{WS}$) and the 0.1M NaOH alkaline extractable HULIS ($HULIS_T$) in atmospheric aerosol collected in an Alpine Valley during winter time. This comparison shows that the simpler DEAE isolation procedure leads to higher recoveries and better reproducibility and should therefore be recommended.

## 1 Introduction

The organic fraction represents an important part of atmospheric aerosols, both from a mass point of view with up to 50% in total mass (Putaud et al., 2004; Pio et al., 2007) and also because it can largely influence physical and chemical properties of particles. Further, the organic fraction can modify the impact of aerosol on the radiative properties of the atmosphere (Kanakidou et al., 2005; Fuzzi et al., 2006) and on human health (Mauderly et al., 2008). The chemical nature of the vast majority of compounds representing the particulate organic matter (POM) remains unknown, with only 10–20% by mass being resolved at a molecular level (Puxbaum et al., 2000). It was recently shown that macromolecular species are important contributors to the unresolved mass of POM, comprising between 10–30% by mass in marine, rural and tropospheric aerosol (Fezcko et al., 2007). This significant fraction is commonly referred to as HULIS (HUmic LIke Substances), because of its physical and chemical similarities with terrestrial and aquatic humic and fulvic acids (Graber et al., 2006, and references therein).

Like humic substances, HULIS can be defined into two major components on the basis of their solubility, namely Water Soluble and Total (WS and T) HULIS. $\text{HULIS}_{WS}$ comprise moderate molecular mass organic substances that are soluble in pure water, whereas $\text{HULIS}_{T}$ also includes higher molecular mass substances only soluble in alkaline media (pH=13, e.g. in 0.1 M NaOH, following conventional humic substances extraction procedure for soil samples). By definition $\text{HULIS}_{T}$ can be directly extracted with 0.1M NaOH.

It is proposed that $\text{HULIS}_{WS}$ represents an important amount of the Water Soluble Organic Carbon (WSOC) mass, up to 30–50% in rural (Havers et al., 1998; Zappoli et al., 1999; Facchini et al., 1999; Decesari et al., 2001; Kiss et al., 2002), urban (Sullivan et al., 2006; Krivacsy et al., 2008; Salma et al., 2008), marine (Cavalli et al., 2004), and biomass-burning aerosol (Mayol-Bracero et al., 2002; Decesari et al., 2006). A large focus is recently directed toward the understanding of WSOC, which presents several specific interests for the study of the physical properties of atmospheric particles and their interactions with clouds. It has been shown that $\text{HULIS}_{WS}$ may affect aerosol properties such as their light absorption (Hoffer et al., 2006; Dinar et al., 2008) and hygroscopicity (Gysel et al., 2004; Badger et al., 2006; Dinar et al., 2006). Therefore, the nature and the abundance of $\text{HULIS}_{WS}$ compounds can significantly influence the cloud condensation ability and thus have a climatic indirect effect.

The isolation or extraction of HULIS from atmospheric particles is currently performed with several techniques that are often adapted from previous researches on terrestrial humic substances (Pavel et al., 2003). Solid-phase extraction, as well as reversed phase, ion exchange, and size-exclusion chromatography have been employed for HULIS separation. These various chromatographic methods fractionate organic compounds on the basis of their molecular weight (Krivascy et al., 2000; Andracchio et al., 2002; Sullivan et al., 2006a), of their polarity (Varga et al., 2001; Andracchio et al., 2002; Duarte et al., 2005; Sullivan et al. 2006b), of their acidity (Havers et al., 1998; Decesari et al., 2000), or the combination of these two last properties (Limbeck et al., 2005). A synthesis is recently proposed by Graber et al. (2006), describing the advantages and the limitations of all these methods. Ultimately, it is however expected that these different methods will extract different compounds with chemical properties dependent on the isolation method itself. There is currently a lack of a unified approach leading to a common operational definition for HULIS in the field of aerosol science. Further, it is difficult to evaluate if the different protocols in use quantify a comparable fraction of POM, because inter-comparisons have never been conducted. Lukacs et al. (2007) proposed the first comparison of the concentration of macromolecular compounds extracted according to a method used by Fezcko et al. (2007) and a second method used by Varga et al. (2001). The latter method isolates more compounds than HULIS, and this fraction characterised as light absorbing organic matter is referred to as "brown carbon" by Andrea and Gelencser (2006).

With the goal to help in the standardization of extraction and quantification methods for atmospheric HULIS, this paper presents, to the best of our knowledge, the first quantitative comparisons of two of the main methods in use. The first one is a single step separation technique using the weak anion exchanger resin DEAE cellulose, while the second one is a two step protocol with separations performed on hydrophobic $C_{18}$ followed by anion exchanger columns. These two methods are compared in order to determine their analytical performances (such as extraction yield and selectivity). They are further applied on a set of atmospheric samples obtained during winter time in an Alpine urban site in order to show their differences.

## 2 Experimental section

### 2.1 Isolation of total and water soluble HULIS

Isolation in one step by anions exchange resins exploits the fact that humic solutions possess an acidic character. The material mainly used in humic research is the DEAE cellulose (Peuravuori et al., 2005) which is a weak anion exchanger with tertiary amine functional groups bounded to a hydrophilic matrix. This technique was adapted to atmospheric research by Havers et al. (1998) to isolate the Total HULIS fraction. Decesari et al. (2000) proposed an improvement of this method also employing an isolation by chromatography on a DEAE TSK gel to split the WSOC into three classes of compounds: neutral and basics compounds, mono- and di-carboxylic acids, and polyacids. The advantage of the use of a DEAE resin is the significant recovery of organic matter (Peuravuori et al., 2005), the ability to inject sample without preacidification, and the possibility to split the water soluble compounds into different chemical classes with only one extraction step. The drawback is that compounds on DEAE cellulose elute only with high ionic strength solution, introducing potential interferences for the quantification or characterisation of HULIS in the extract.

Limbeck et al. (2005) proposed a more complex method to isolate the HULIS fraction in aerosol samples based on the protocol proposed by Varga et al. (2001). This improved method includes a second extraction step with an anion exchanger column. Therefore, it includes a separation performed in two steps, the first one based on polar interactions with $C_{18}$ resin, the second one using the acidic nature of HULIS for separation with a SAX strong anion exchanger. The combination of these two extraction steps with two different mechanisms provides high selectivity towards HULIS, which is the major advantage of this protocol. These two methods together cover approximately half of the current work about HULIS quantification (Decesari et al., 2000; Varga et al., 2001; Duarte et al., 2005; Limbeck et al., 2005; Sullivan et al., 2006b) and have been applied to a great variety of atmospheric samples. They dominate in terms of simplicity, selectivity, and redundancy in the literature. They were tested in our laboratory for comparison of their results for $HULIS_{WS}$ and $HULIS_{T}$.

### 2.1.1 DEAE resin

We implemented at Laboratoire de Glaciologie et Géophysique de l'Environnement the protocol proposed by Havers et al. (1998). The Total or Water Soluble fractions obtained from aerosol samples (see Sect. 2.5) are passed through the DEAE column (GE Healthcare®, HiTrap$^{TM}$ 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 6 mL of organic free water (Elga) to remove neutral components and hydrophobic bases. Then, mono- and di-acids together with some anionic inorganic species retained in the resin are eluted with 12 mL of a solution of NaOH 0.04 M (J. T. Baker®, pro analysis). Finally, the polycharged compounds (the HULIS) are quickly eluted in a single broad peak using 4 mL of a high ionic strength solution of NaCl 1 M (Normapur). All flow rates are set at 1.0 mL min$^{-1}$. This last fraction is preserved for carbon quantification (see Sect. 2.2).

### 2.1.2 $C_{18}$+SAX resins

The methodology of the whole isolation procedure was published by Limbeck et al. (2005) and was implemented at LGGE. In summary, the first solid phase extraction step is performed on a $C_{18}$ SPE column (IST, 221-0020-H) (I cm ID, length 6.0 mm). The filtered liquid extract obtained from aerosol samples is adjusted to pH 3 with a solution of $HNO_3$ (Merck®, 65%, pro analysis) and passed through the sorbent column. Then, 1 mL of water is used to remove inorganic and organic compounds not retained on the sorbent. The adsorbed fraction is further eluted with 400 $\mu$L of methanol (J. T. Baker®, MOS Grade). This last extract is diluted with water and acidified with $HNO_3$ to obtain 2.8 mL of solution at pH=3. To limit interferences with methanol during the second separation step, only 1 mL of this solution is injected though the SAX adsorbent (Isolute SAX, IST 500-0020-H) contained in a Teflon® microcolumn (I.0 mm ID, length 15.0 mm). After this concentration step, the column is washed at a flow rate of 0.6 mL $min^{-1}$ with 2.4 mL of water, to remove neutral compounds. The HULIS fraction is further eluted from the resin at a flow rate of 0.6 mL $min^{-1}$ with 3.6 mL of a solution of $NH_4OH$ (0.05 M) (Sigma-Aldrich®, ACS reagent).

## 2.2 Isolation of total and water soluble HULIS

Two different types of detectors are used in the literature for the quantification and the characterisation of the HULIS fraction, namely direct carbon measurements with TOC analysers, and spectroscopic methods. Quantification of humic substances has been mainly approached by UV spectroscopic methods, owing to their simplicity and rapidity. In the field of aquatic researches on humic substances, various wavelengths had shown important correlation between absorbance and carbon concentrations measured with DOC analyzers, i.e. 250, 254, 285, 330, and 350 nm (Hautala et al., 2000). For the accurate calibration needed for the quantification, UV-Visible spectroscopy requires standard compounds with optical properties identical to that of the samples. Chromophores responsible for the absorbance of humic substances are conjugated double bonds (conjugated system, aromatic rings) as well as functional groups like ketones, amines, or nitrated derivatives. Absorbance of such samples increases with pH, aromaticity, total carbon content, and molecular weight (Chen et al., 1977). However, characteristics of HULIS may largely differ from that of humic substances, generally showing a smaller average molecular weight and lower aromatic moiety content (Graber and Rudich, 2006). Hence, because exact standard compounds do not exist for HULIS (see Sect. 2.3), the calibration performed with UV spectroscopy using humic and/or fulvic acids as reference compounds can introduce large errors for the quantitative determination of HULIS concentrations. Finally, the direct quantification of carbon content with DOC analyzers is much preferred and will be used in this study. Yet, as spectroscopy can provide useful information on the chemical structure of HULIS, UV-Vis spectra are acquired during the separation procedure. It should be noted that quantification with DOC methods requires that the oxidation of HULIS is complete during the analytical step. We implemented both methods for the quantification and characterization of HULIS. UV-Vis measurements are performed on-line after the extraction systems, using a diode array detector (Dionex UV-VIS 340U), and recorded in the range 220–550 nm. The HULIS fractions are subsequently collected manually and the carbon content is analyzed with a DOC analyser (OI Analytical 700 TOC Analyser) after chemical oxidation of the organic matter. The detailed protocol is described elsewhere (Jaffrezo et al., 2005). Briefly, the inorganic carbon is first eliminated after acidification (600 $\mu$L of ortophosphoric acid, 5% in volume, Normapur®, analytical reagent) of the sample and the $CO_2$ formed is removed in a $N_2$ stream. This step is followed by a warm oxidation using persulfate (Normapur®, CL00.1402.1000, 100 g.L$^{-1}$) and the $CO_2$ resulting from organic matter oxidation is measured by a non dispersive infrared spectrophotometer. The calibration is performed with potassium hydrogen phthalate (GRP Rectapur) for carbon concentration in the range of 0–2 ppmC. Since the chloride anion inhibits the oxidation reaction, the DEAE extract is diluted by a factor two and the oxidant volume introduced in the reactor is in large excess (6 mL). The usual volume of oxidant (1 mL) is used for the quantification of the carbon mass in extracts obtained with the $C_{18}$+SAX method. Measurements of WSOC concentrations in aerosols samples are also conducted with this device (Jaffrezo et al., 2005) (see Sect. 2.4).

### 2.3 HULIS Standard

The comparison of the results obtained with DOC and UV-Vis methods requires a proxy standard for HULIS compounds that is commercially available. Two products are commonly used in the literature as model compounds for atmospheric HULIS, Suwannee River Fulvic Acid (SRFA) and Humic Acid from Fluka®. The SRFA obtained from the IHSS (product number 1R101F) is used in many studies as a proxy for atmospheric $HULIS_{WS}$ (Fuzzi et al., 2001; Brooks et al., 2004; Chan et al., 2003; Kiss et al., 2005; Samburova et al., 2005; Hopkins et al., 2007; Hatch et al., 2008). Humic Acid from Fluka (53680) is used by Limbeck et al. (2005) and Fezcko et al. (2007) for TOC and procedure calibrations. Based on spectroscopic, elemental, $^{13}$C-RMN, $^{1}$H-RMN, and FTIR-ATR studies of the respective chemical composition of atmospheric HULIS and aquatic humic substances, it is shown that both compounds comprise similar carbon functional groups (Havers et al., 1998; Krivacsy et al., 2001a; Duarte et al., 2004, 2005; Tagliavini et al., 2005; Sambrurova et al., 2007) but differ in terms of their relative H/C and O/C ratio. WSOC hydrophobic acids (HULIS) show a higher aliphatic structure and a lower degree of oxidation than those of humic substances (Graber and Rudich, 2006; Duarte et al., 2007). Therefore, aerosol WSOC hydrophobic acids are found to be only qualitatively similar to aquatic humic substances.

Because SRFA is mainly used as standard in the literature and $\mathrm{HULIS}_{WS}$ is by definition composed mainly of fulvic acids, we also choose, like many other groups, to evaluate both protocols with SRFA to represent HULIS fractions in our study. However, some experiments were also performed with Humic Acid Fluka, in order to compare our results with those of Limbeck (2005). All of these evaluations are conducted with volumes of solutions leading to carbon loads between 5–15 $\mu$gC of SRFA and humic acids for the DEAE protocols, and in the range 10–25 $\mu$gC for the $C_{18}$+SAX protocol, in the range of the carbon load encountered in actual aerosol samples extracts. Humic acid and Fulvic acid solutions were prepared by dissolving an amount of dried products in organic free water (Elgastat). Ultrasonic agitation was used for both preparations in order to get a complete dissolution. The Humic acid solution was filtered trough an Acrodisk filter to eliminate insoluble particles.

## 2.4 Aerosol sampling

After characterisation (see Sects. 3.1 and 3.2), the methods were applied to a series of actual atmospheric samples. Sampling took place in the Chamonix valley, in the French Alps. The sampling site was located in the suburban area of the Chamonix town (6°52′16″ E; 45°16′34″ N; altitude 1038 m a.s.l., about 20 000 inhabitants in winter), in a grassy area about 60 m from a road. The 15 km long valley floor is rather flat at an elevation of approximately 1000 m a.s.l. on average and is surrounded by tall mountains culminating with the summit of Mont Blanc (4810 m a.s.l.). There are neither industrial emissions nor waste incinerators in the valley, and the main anthropogenic sources of emissions are vehicular traffic, residential heating (fuel or wood burning stoves) and some agricultural activities. The sampling took place for a period of 10 days in winter 2007 (10–19 December 2007). Sampling duration was based on a day/night pattern, with 12hr sampling starting at 08:00 and 20:00 local time. $PM_{10}$ samples were collected on quartz fiber filters (Whatman®, diameter of 150 mm) with a high-volume sampler (Tisch Andersen) at a flow rate of 30 $m^3 h^{-1}$. After sampling, the filters were wrapped with aluminium foil in sealed polyethylene bags and stored frozen until further analysis. A total of 16 samples and 3 blanks were collected. Air temperature during the campaign ranged between −15.6°C and −3.5°C (average −11.2°C); winds were calm, and no precipitation was recorded. In these conditions, a large share of atmospheric PM is due to local emissions of wood combustion from domestic heating (Marchand et al., 2004).

### 2.5 Aqueous and alkaline extraction of the aerosol samples from quartz filter

The water-soluble fraction of each sample is obtained with the extraction of 12–22 $cm^2$ of filter during 30 min in 9 mL of organic free water (Elgastat) using ultrasonic agitation. The surfaces extracted are adapted to the OC concentrations measured in each sample (see Sect. 2.6). Accordingly, to obtain the alkali-soluble fraction, 12 $cm^2$ of sample are extracted during 1 h in 9 mL of 0.1 M NaOH solution using ultrasonic agitation. After sonication, the extracts are filtered with Acrodisk filters (Pall Gelmann®, 0.22 $\mu$m porosity) to remove any particles in suspension. The solutions are kept frozen before analysis. Measurement of HULIS and soluble OC are performed on both types of solution, water and alkali extracts.

### 2.6 OC/EC quantification

Samples are analyzed for EC and OC using the Thermo-Optical Transmission (TOT) method on a Sunset Lab analyzer (Birch and Cary, 1996; Aymoz et al., 2007). We are using the newly developed EUSAAR2 temperature program proposed in Cavalli et al. (2008). It includes temperature 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% $O_2$. Automatic split time was always used for the distinction between EC and pyrolysed OC. We analyzed fractions of 1.5 $cm^2$ of the filters, without any preparation.

## 3 Results and discussion

In order to determine the respective performances of both methods, different analytical characteristics such as linear range, reproducibility and yield of extraction were studied with SRFA standard solutions. The presence of interfering materials should also be taken into consideration. Recovery tests were carried out with a variety of different water-soluble organic compounds relevant to atmospheric aerosol.

### 3.1 Analytical performance

The extraction yield is defined as the ratio between the concentration recovered and that introduced in the resins, using 20 $\mu$C of a synthetic solution of SRFA. For both methods, recovery is not complete, as a fraction of the analyte remains in the sorbents due to irreversible adsorption (cf. Table 1). In our case, the separation of SRFA on DEAE-cellulose presents a recovery of 93.0±1.1% ($n$=10), comparable to the results of Havers et al. (1998). The recovery on $C_{18}$+SAX leads to a much weaker yield, with an average of 50.8±2.9% ($n$=13). Comparable results are obtained when using UV detection. Limbeck et al. (2005) mentioned a recovery of 70% for the first extraction step of the latter method, as determined with UV detection and humic acid Fluka standard solutions. No value is provided for the whole method to compare with our results. We performed further extraction experiments with humic acids for both methods, in order to compare with values presented by Limbeck et al. (2005). We used loads of 20 $\mu$C of humic acid (Fluka) and measured yields that are much lower with average values about 60±2.2% and 25±3.6%, for DEAE and $C_{18}$+SAX methods, respectively. Therefore, these results indicate more irreversible interactions between the resins and higher molecular weight acidic compounds. Overall, we can conclude that a higher uncertainty can result when correcting the HULIS concentrations measured in actual atmospheric samples for the extraction yield as determined with SRFA for the $C_{18}$+SAX method. However, for both methods, a good correlation was found between DOC response before and after the extraction steps, for a range of loads between 0 and 25$\mu$g C in SRFA. It shows that the performances of both procedures are not influenced by the analyte load in this range.

The reproducibilities of the methods were also determined (see Table 1). For the DEAE method, relative variabilities of 1.0% and 1.7% were obtained for TOC and UV (250 nm) measurements, respectively, for extractions of series of SRFA amounts of 10 $\mu$gC ($n$=7). For the $C_{18}$+SAX method, a series of measurements of SRFA amounts of 20 $\mu$gC ($n$=7) led to a relative variability of 5.7% with the DOC analyser and 9.4% with UV detection. Limbeck et al. (2005) showed a similar value (i.e. 4.3%) using a more automated system. Therefore, particularly for the former method, the reproducibility is excellent down to amounts allowing the measurements of low atmospheric concentrations.

The limits of detection (LOD) were calculated as twice the standard deviation of the blank value obtained for each procedure for series of 10 measurements performed with Elgastat® water. The average blank values are about 0.60 $\mu$gC and 1.50 $\mu$gC for the DEAE and $C_{18}$+SAX methods, respectively. We found LOD of 0.5 $\mu$gC for the DEAE method and 1.7 $\mu$gC for the $C_{18}$+SAX method, as determined with the DOC detection. The larger LOD for the latter method is due to both successive separation steps that imply a larger irreversible and variable adsorption of the analyte, as seen before. More-over, in order to limit the interferences with methanol during the separation on the SAX resin, the $C_{18}$ extract is not fully injected, further increasing the LOD. It should be mentioned that such LOD can only be achieved after several sequences of initial washing of the brand new resins, with water and methanol for $C_{18}$ and SAX solutions, and with water for DEAE, in order to get a low and stable background blank value. Also, for both methods, successive uses of the resins for the analyses of actual samples modify the overall background blank value. To avoid errors on the measurements, a blank of the whole procedure is performed after each couple of samples and the resins are discarded after every set of approximately 40 samples.

### 3.2 Selectivity tests

HULIS consists in polyfunctional compounds made up of a heterogeneous mixture of aliphatic and aromatic structures with substituted acidic, phenolic, methoxy, and ester functional groups (Decesari et al., 2001; Krivacsy et al., 2001; Kiss et al., 2002; Mayol-Bracero et al., 2002; Graber and Rudich, 2006; Samburova et al., 2007). Organic compounds present in aerosol can potentially influence the performance of the separation and quantification techniques as soon as they contain such functional groups. In the isolation protocol of Varga et al. (2001), some interfering compounds like fatty acids, long chain monocarboxylic acids, and aromatics alcohols remain in the isolated fraction (Lukas et al., 2007; Salma et al., 2008). Such a lack of selectivity is also mentioned when $XAD_8$ resin is used, since phenols, aromatic acids, and cyclic acids co-elute with humic substances in this case (Sullivan et al., 2006b). In the protocol proposed by Decesari et al. (2000) using DEAE, phenols elute in the polyacids fraction, as also demonstrated by Chang et al. (2005). Decesari et al. (2005, 2006), and Mancinelli et al. (2007) proposed a more selective protocol using DEAE but the carbonaceous composition of the eluent prevents the measurement of the carbon content with a DOC analyser. A further improvement using an elution protocol with inorganic compounds to allow for DOC analyses is proposed by Mancinelli et al. (2007) but in this case some phenols and other interfering compounds co-elute with polyacids.

To characterize the selectivity of both extraction methods studied, recovery tests were performed for many different organic and inorganic compounds comprising functional groups commonly found in HULIS. Table 2 summarizes the results obtained with standard solutions for loads of 20 $\mu$C of each compound. On the one hand, we can see that none of these chemical species elute in the fraction of interest for either extraction method, and can therefore interfere with our target compounds. On the other hand, both standard compounds elute entirely in the expected fractions, collected for further quantification. Phenols, which present the principal interfering compounds for different protocols, do not co-elute in the extracted fractions. Therefore, it can be concluded that these two methods are fully selective toward humic-like compounds.

### 3.3 Determination of HULIS in aerosol samples

The mass concentrations of HULIS were determined with DOC measurements in the aqueous and alkaline extracts of the actual aerosol series collected in Chamonix and quantified. UV spectroscopy was also conducted in order to gain some insights on the characterisation of the extracted HULIS. Results are corrected for the extraction yields obtained with SRFA, and expressed in HULIS equivalent carbon mass concentrations in the atmosphere ($\mu$gC.m$^{-3}$). Field blanks were negligible compared to the concentrations of actual atmospheric samples, as measured with the DEAE and $C_{18}$+SAX methods.

Results obtained for HULIS$_{WS}$ and HULIS$_{T}$ with both methods are presented in Fig. 1. It reveals that the $C_{18}$+SAX method is more discriminating than the DEAE method for HULIS$_{WS}$, with much lower concentrations obtained with the former. This result is also in line with the much lower yield obtained for $C_{18}$+SAX with SRFA, and may indicate that extraction yield for actual HULIS is even lower than measured for SRFA and used to correct the measured HULIS concentration. Conversely, results for HULIS$_{T}$ are nearly equivalent for both methods.

The really good correlations between both methods for both types of HULIS most probably indicate a stability of the characteristics of HULIS during most of the period of the study, together with stable extraction procedures in these concentration ranges, as already mentioned earlier. However, some points are not aligned on the regression lines even taking into account the uncertainties associated with the measurements, an indication that some of the samples are slightly different in their chemical composition. Further, it should be noted that both regressions show negligible intercepts, an indication that there is no systematic error due to erroneous blank corrections. The comparison between the concentrations of $\text{HULIS}_T$ and $\text{HULIS}_{WS}$ is presented later (see Sect. 3.5).

The comparisons between the quantifications performed with DOC measurements and the results obtained at the same time with the UV detection at 250 nm are presented in Table 3, both for $\text{HULIS}_{WS}$ and $\text{HULIS}_T$ in the actual atmospheric samples, and for the reference compound SRFA in the range 3 to 20 $\mu$gC. We choose 250 nm as a reference wavelength because of the large sensitivity obtained for SRFA for this wavelength, associated with the large density of aromatic structures in this compound (see Sect. 3.4.b). A close correlation can be found between both series of measurements, in every case investigated. Correlations are in each case larger for the DEAE method than for the $C_{18}$+SAX method, an indication that the extraction with the former method better preserve the functional groups responsible for the absorbance at 250 nm. Note that correlations are also better for the reference compound than for the actual extracts, but that the differences are small between the reference and the $\text{HULIS}_T$ extracts. Finally, these good correlations calculated with the overall actual samples series are again an indication that both types of extracted HULIS present rather stable characteristics during the whole sampling period. All of the intercepts are rather small, representing the absorbance of a few tenths of $\mu$gC at most. The slopes of the regression are always higher for the $C_{18}$+ SAX than for DEAE method, and we can infer that the extract from $C_{18}$+ SAX method presents a stronger specific absorbance.

### 3.4 Qualitative observations deduced from spectroscopic measurements

Some insights can be gained with spectroscopic investigations in order to explain the observations above, since light absorption in the UV-Vis range is a typical property of humic substances. This technique cannot deliver detailed information about the chemical structure of HULIS but it can provide results for comparative studies of the isolated fractions. It is based on some widely used quantitative parameters: the absorbance data measured at 254 and 280 nm, calculated per mass unit of carbon (the specific spectral absorbance), and ratios of spectral absorbance measured at 254 and 360 nm ($E_2/E_3$ ratio).

#### 3.4.1 UV-Visible spectra

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. A shift in the UV spectra to an absorbance above 300 nm suggests that poly-conjugated and polymeric structures are present. Indeed, the presence of aromatic and conjugated compounds, the main electron sources, explains the shoulder that can be found in humic substances spectrum (Domeizel et al., 2004). Absorbance in the bands between 270–280 nm is related to electron transitions in phenolic arenes, aniline derivatives, polyenes, and polycyclic aromatic hydrocarbons with two or more rings. These compounds are supposed to be common structural subunits in humic matter (Traina et al., 1990).

We can compare UV spectrum of a SRFA water standard solution before and after extraction with both protocols (cf. Fig. 2). For comparison, each absorbance spectrum was plotted by normalizing the UV-Vis absorbance to the mass of carbon in the extracted HULIS. It is obvious that the DEAE protocol, respecting both the structure of the absorption spectrum and the absorption efficiency, do not change the nature of the standard. Conversely, the $C_{18}$+SAX extraction protocol strongly changes the shape of the spectrum with a much higher specific absorbance at 250 nm and a pronounced shoulder between 300 and 350 nm. It can be concluded that this last protocol favours the extraction of high UV-absorbing compounds (i.e., aromatic and conjugated systems).

Figure 3 presents UV-Vis spectra of both $\mathrm{HULIS}_T$and $\mathrm{HULIS}_{WS}$ extracts from one actual sample of our atmospheric series. The general shapes of the extracts obtained with the DEAE protocol are rather similar to that of SFRA, as shown in Fig. 2, with only slightly larger specific absorbance in the shorter wavelengths region (<400 nm).The differences in the spectra of $\mathrm{HULIS}_T$and $\mathrm{HULIS}_{WS}$ are not very large, and limited to the 250–340 nm region where a larger absorbance indicates a slightly increased concentration of aromatic and high molecular weight polymeric compounds in the former extract. Conversely, the differences are much larger with both WS and $T$ extracts isolated with the $C_{18}$+SAX protocol, the specific absorbance of the latter extracts being much larger over a very large range of wavelengths (250–450 nm) again associated with aromatic and high molecular weight polymeric compounds. Overall, these results again indicate that the $C_{18}$+SAX method tends to favour the specific extraction of short UV-absorbing compounds compared to the DEAE method.

### 3.4.2 Specific absorbance

In the field of humic substance research, absorbance values at 280 nm and 254 nm are commonly used for the calculation of molar absorptivities. For reasons previously explained (see Sect. 3.4.a), the wavelength of 280 nm was chosen by Chin et al. (1994) and by Peuravuori and Pihlaja (1997) for such studies on humic substances. Schafer et al. (2002) prefer to use 254 nm because most of the aromatic structures present strong absorption near 250 nm. These spectroscopic parameters permit evaluation of the abundance of UV absorbing chromophores. From our spectrum, we measured molar absorptivities for the different isolated HULIS fractions at 280 nm and 254 nm (Table 4).

This table indicates that for a given wavelength and a given method, the specific absorbance of the three extracts are in the same range, an indication that each method is providing extracts including a homogeneous mixture of compounds independent of the original sample. Also, the specific absorbance of SRFA is largely increasing after extraction, in larger proportion for the $C_{18}$+SAX method. Therefore, the extractions are selectively leading to compounds with larger absorbance and/or lower carbon content, and this selectivity is more pronounced for the $C_{18}$+SAX method. Finally, the difference is small between the specific absorbance of $HULIS_T$ and $HULIS_{WS}$ while the former are supposed to present larger molecular weight. Therefore, this mass increase is probably associated with a larger absorbance, leading to a stable specific absorbance.

### 3.4.3 Aromaticity indicator

The ratios between the respective absorbance at two wavelengths can give useful information and is commonly used in the field of aquatic research to perform comparisons between samples. The ratio between the absorbances at 250 and 365 nm (noted $E_2/E_3$) decreases when the aromaticity and/or molecular size of aquatic humic solutes increase (Peuravuori and Pihlaja, 1997). The determination of $E_2/E_3$ ratio for HULIS has also been approached by Duarte et al. (2007) and Krivacsy et al. (2008). However, it is not possible to proceed to comparisons with our results due to differences in pH conditions of the extracts leading to changes in specific absorbances. The ratios determined in our study are presented in Fig. 4.

SRFA present a higher ratio than HA compounds. In agreement with their chemical definition this result shows that HA present more aromatic and/or higher molecular mass compounds than SRFA. The same parallel can be made with $HULIS_T$ and $HULIS_{WS}$. $HULIS_T$ present smaller ratio than $HULIS_{WS}$ due to higher molecular mass substances and/or more aromatic system. The structural compositions of the standard mixtures extracted with both protocols slightly differ from the one of the original compound. Comparing the wavelength ratio for SRFA and its extracts by both methods show that these do not discriminate the same kind of compounds. With a higher ratio after extraction, the $C_{18}$+SAX protocol discrimates towards smaller or less aromatic molecules. As we have seen (Sect. 3.4.2) that this extract tends to be enriched in aromatic systems, it most probably leads to irreversible adsorption of the larger molecular weight compounds of the standard mixture. The compounds extracted are probably high absorbing UV compounds (high absorbing value at 250 nm) (see Sect. 3.4.a) but with small molecular weight (weak absorbing value at 360 nm). Conversely, the lower ratio after the DEAE extraction implies that the compounds that are lost are less aromatic or have lower molecular weight than the average HULIS.

The average ratios $E_2/E_3$ for the atmospheric samples extracted with both methods show important differences with that of SRFA, with larger ratios for the latter. However, it is expected that HULIS, with smaller average molecular weight and lower aromatic moiety content (Graber and Rudich, 2006) compared to fulvic acids, should presents higher ratios $E_2/E_3$. The lower values observed in our case could tentatively be explained by the large impact of biomass burning, with emissions of aromatic compound (structures derived from lignin compounds) or by a slower degradation of aromatics in winter (Samburova et al., 2007).

### 3.5 Discussion of atmospheric concentrations

Concurrent measurements of OC, WSOC, and HULIS concentrations during the field campaign allow several observations on the links between these different properties. First of all, there is a very strong connection between OC and WSOC ($\mathrm{WSOC}=0.49\times\mathrm{OC}+0.18$; $R^2=0.94$; concentrations in $\mu$gC.m$^{-3}$). This excellent correlation is again an indication of the stability of the nature of particulate organic matter (POM) during the overall sampling campaign, including stability between day and night periods. This is further confirmed by the very small intercept most probably related to a dominant source for OC (i.e. biomass combustion) at this period of the year. This is further in line with the high proportion of WSOC found for a winter period. Similar observations were already reported for the same site (Jaffrezo et al., 2005).

Figure 5 presents the correlations between the concentrations of OC, WSOC, and $\mathrm{HULIS}_T$ and $\mathrm{HULIS}_{WS}$ obtained with the DEAE protocol. Figure 6 presents the same results for HULIS fractions obtained with the $C_{18}$+SAX protocol. Figure 5 indicates excellent correlation coefficients between the concentrations of both types of HULIS extracts and OC, and between $\mathrm{HULIS}_{WS}$ and WSOC. Again, the intercepts are negligible in all cases. This shows again that the concentrations of all these constituents varied in a coherent manner during the overall campaign, including day and night periods. Most probably, this can be attributed to a stable and dominant source of POM in the valley. The contribution of $HULIS_{WS}$ to WSOC measured in our study are comparable to data obtained in similar environments, with ratios reported between 24–44% for polluted rural background (Decesari et al., 2001), and ratios of 25±6% for tropical biomass burning aerosol (Mayol-Bracero et al., 2002). Finally, Fig. 5 indicates a contribution of $HULIS_{WS}$ to $HULIS_T$ of about 45 %, underlining the importance in terms of mass and composition of the alkali soluble fraction in these conditions. The relative contribution of $HULIS_{WS}$ (in biomass burning aerosol) to light absorption in the entire solar spectrum is around 7%. The principal contribution (up to 50%) to light absorption is at 300 nm (Hoffer et al., 2006). So $HULIS_T$, which present similar optical properties (see Sect. 3.2), can be expected to have an even more active role in radiative transfer and photochemistry.

Figure 6 shows that the $C_{18}$+SAX protocol leads to a larger dispersion of the results, with correlation coefficients between the same parameters much lower than those obtained above with the DEAE method. They are however still significant, and intercepts are still negligible. The variability in the results can probably be attributed in part to the lower reproducibility of the method (see Sect. 3.1), but also to some extent to chemical variability in the fraction extracted, that translates in a variable extraction efficiency. In our tests (see Sect. 3.1.) we measured extraction efficiency varies from ∼50% for SRFA (value used for correction) to ∼25% for HA. As mentioned earlier (Sect. 3.3), the fractions of OC ascribed to both types of HULIS using this extraction protocol is lower than that deduced with the DEAE method. It should be mentioned that the ratios HULIS/WSOC and HULIS/OC are rather low if the yields are corrected with SRFA, while they significantly increase when HA is used for the correction. In this last case, a contribution of 16.3±3.8% is obtained for $HULIS_{WS}$/OC, comparable to the results obtained by Limbeck et al. (2005) for sampling in the cold season in urban background, with an average contribution of $HULIS_{WS}$ to the organic fraction of 13.7%. Such questions do not really exist for the DEAE procedure for which a very good recovery (97%) of SRFA is observed.

## 4 Conclusions

HULIS are a major contributor to the organic carbon fraction in atmospheric aerosols. It would be necessary to define a standardized analytical method that could be easily and routinely used for the determination of the concentrations of HULIS in the field of aerosol sciences. The objective of the present work was to compare the characteristics of two of the main methods in use, the DEAE and $C_{18}$+SAX methods. In this work, these two protocols have been applied to determine two HULIS fractions, the water extractable fraction and the total extractable fraction in alkali media, both for standard compounds (SRFA and HA), and for actual aerosol collected in winter.

A significant advantage of the DEAE procedure is that the isolation of HULIS from atmospheric samples is possible without any preacidification. This method may be directly applied to the aqueous and alkali extract aerosol. This isolation procedure is simple (in one step), reliable, and selective and the high extraction yield provides a detection limit of 2 $\mu$gC, as determined with SRFA. The high recovery of this method can provide extensive information on the HULIS structure. The drawback of this method is the high ionic strength used during the final elution that does not facilitate the HULIS quantification. Also, the physical and chemical characterisation of HULIS compounds may be difficult due to interferences with this inorganic eluent.

For a given sample, the quantity and structural composition of the HULIS obtained by the $C_{18}$+SAX method strongly differ from that obtained with the DEAE method. Particularly, this method presents half the extraction yield of DEAE for both standards compounds (SRFA and HA), leading to a larger detection limit of 8 $\mu$gC for SRFA. However, like for the DEAE method, the efficacy of the two separation steps is not affected by the presence of potentially interfering organic matrix. In turn, the UV measurements have shown that this method is strongly selective toward UV absorbing compounds and appears to be discriminatory for the HULIS fraction itself.

As a result, DEAE extraction should be recommended owing to more consistent extractions and sturdier results. However, further investigations on the difference between the two methods may be required, including extensive characterisation and quantification studies on a wide variety of aerosol samples coming from different emission sources.

## 5 Notation

| | |
|---|---|
| ASOC | Alkali Soluble Organic Carbon |
| DEAE | DiEthylAminoEthyl |
| EC | Elementary Carbon |
| $\text{HULIS}_T$ | Total HUmic LIke Substances |
| $\text{HULIS}_{WS}$ | Water Soluble HUmic LIke Substances |
| OC | Organic Carbon |
| POM | Particulate Organic Matter |
| SRFA | Suwanee River Fulvic Acids |
| WSOC | Water Soluble Organic Carbon |

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**Table 1.** Analytical performances of both methods.

| | DEAE | | $C_{18}$+SAX | |
|---|---|---|---|---|
| Analyser | TOC | UV (250nm) | TOC | UV (250nm) |
| Range studied ($\mu$gC) | 3–20 | | 5–20 | |
| Limit of detection ($\mu$gC) | 0.4 | 4.2 | 1.7 | 10.6 |
| Extraction yield ($n$=10) (%) | 93.0±1.1 | 96.0±2.0 | 50.8±2.9 | 52.5±8.1 |
| Relative standard deviation ($n$=10) (10$\mu$gC) (%) | 1.2 | 1.7 | 5.7 | 9.4 |

**Table 2.** Chromatographic separation of single standard compounds.

|  | DEAE |  |  | $C_{18}$+SAX |  |
|---|---|---|---|---|---|
| Functional group and Compounds | Eluted with $H_2$0 | Eluted with NaOH | Eluted with NaCl | Not retained | Retained |
| Carbonyls |  |  |  |  |  |
| -Methyl glyoxal | X | X |  | X |  |
| -Propanal | X |  |  | X |  |
| -Butyraldehyde | X |  |  | X |  |
| Phenols |  |  |  |  |  |
| -Phenol | X |  |  | X |  |
| -Vanillin |  | X |  | X |  |
| -Syringaldehyde |  | X |  | X |  |
| -Salicylic acid |  | X |  | X |  |
| Aromatic Acids |  |  |  |  |  |
| -Benzoic acids |  | X |  | X |  |
| Amine |  |  |  |  |  |
| -2,3Diaminonaphthalene | X |  |  | X |  |
| Saccharide |  |  |  |  |  |
| -Levoglucosan | X |  |  | X |  |
| Humic Substances |  |  |  |  |  |
| -SRFA |  |  | X |  | X |
| -Humic Fluka |  |  | X |  | X |
| Anions |  |  |  |  |  |
| -Nitrate |  | X |  | X |  |

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Interactive Discussion

**Table 3.** Correlations between TOC ($x$, $\mu$gC) and UV (y, mAU) data at 250 nm.

| | | DEAE | | $C_{18}$+SAX | |
|---|---|---|---|---|---|
| Wavelength | Analyte | Regression | $R^2$ | Regression | $R^2$ |
| 250 nm | SRFA ($n$=10) | 46.6x+26.2 | 0.99 | 79.8x+13.5 | 0.96 |
| | $HULIS_{WS}$($n$=15) | 54.6x+11.5 | 0.94 | 80.0x+19.8 | 0.88 |
| | $HULIS_T$($n$=14) | 60.1x−18.8 | 0.96 | 85.0x+21.5 | 0.90 |

**Table 4.** Specific absorbance of different analytes for both procedures at 254 nm and 280 nm.

| | DEAE | | $C_{18}$+SAX | |
|---|---|---|---|---|
| Analyte | 254nm | 280nm | 254nm | 280nm |
| SRFA | 52.1±3.0 | 34.5±1.4 | 87.7±7.0 | 65.12±4.5 |
| $HULIS_{WS}$ | 58.9±6.5 | 40.6±4.3 | 94.9±14.8 | 66.2±10.8 |
| $HULIS_{T}$ | 59.5±5.9 | 43.5±3.4 | 97.2±14.0 | 77.3±10.5 |
| SRFA w/o extraction | 39.8±1.0 | 27.4±1.0 | 39.8±1.0 | 27.4± 1.0 |

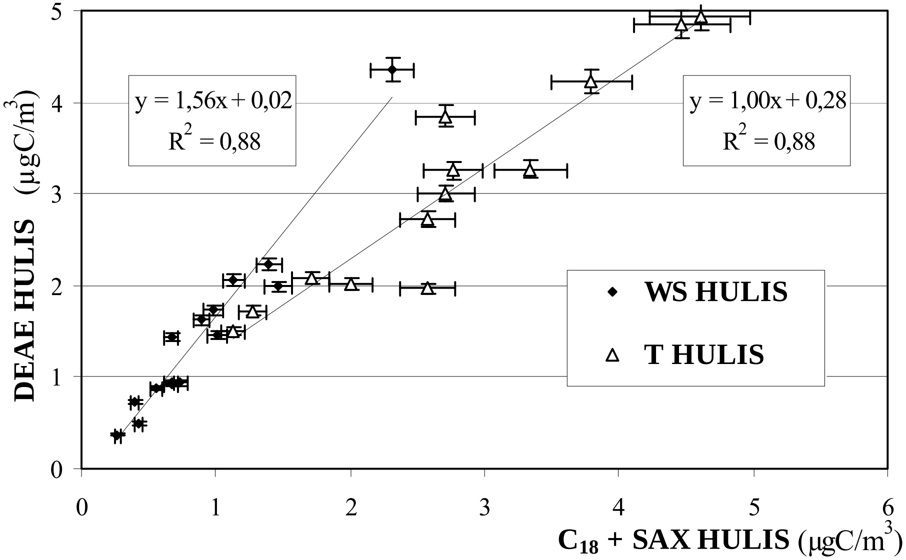

**Fig. 1.** Variations of concentrations of Total HULIS and Water Soluble HULIS (in $\mu$gC.m$^{-3}$) as determined by DEAE and C$_{18}$+SAX protocols and TOC measurements. Uncertainties include relative standard deviation of extraction efficiency determined for both methods with SRFA standard.

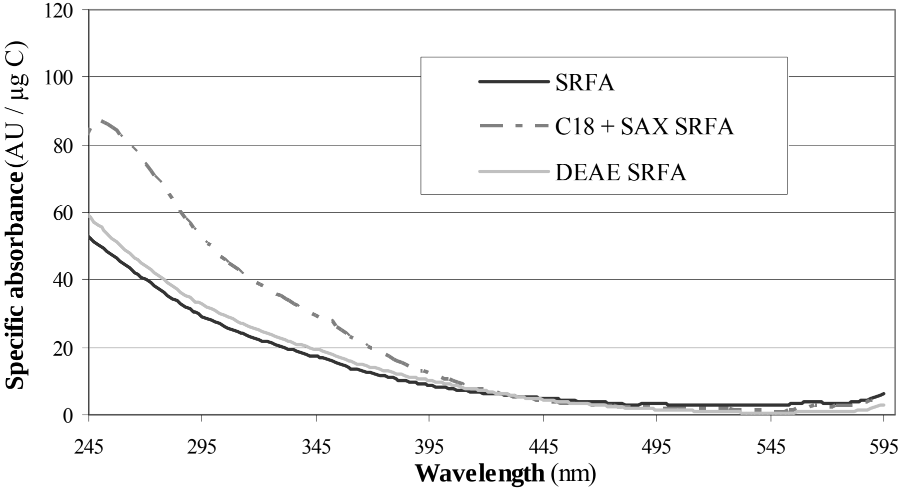

**Fig. 2.** Impact of the DEAE and $C_{18}$+SAX extraction protocols on the UV spectrum of a SRFA standard solution. Specific absorbance is in arbitrary unit (AU) of absorbance per $\mu$g carbon extracted

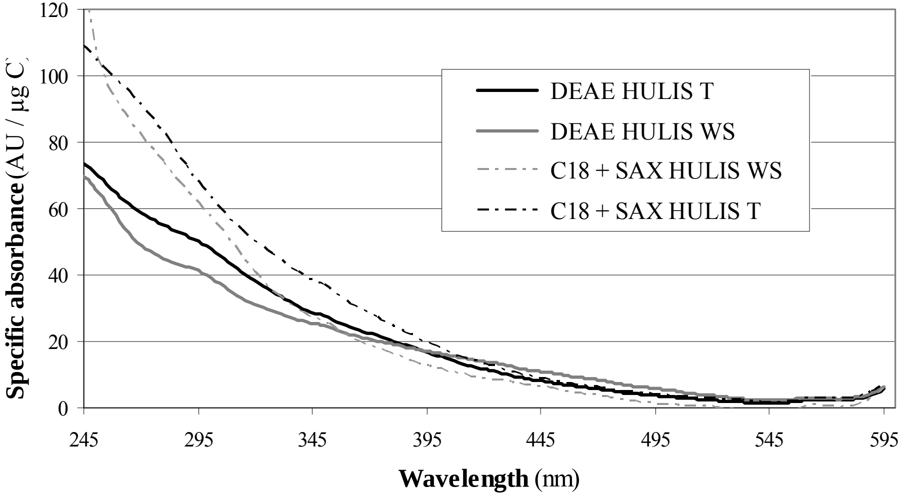

**Fig. 3.** Comparison of the Water Soluble and Total HULIS spectra resulting from both extraction procedures for an actual atmospheric sample. Specific absorbance is in arbitrary unit (AU) of absorbance per $\mu$g carbon extracted.

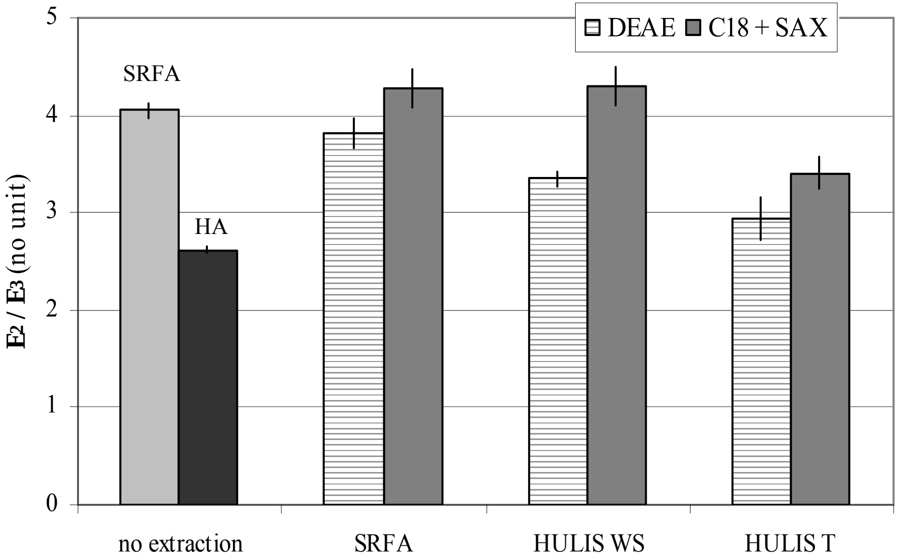

**Fig. 4.** Absorptivity ratios between 250 nm and 365 nm. Comparison of wavelength ratio for humic standard SRFA and its extract by both methods with HULIS extracts. Pure HA is included because it is used as a calibration standard by Limbeck et al. (2005). Uncertainties include standard deviation on the sample set or standard solutions analysed.

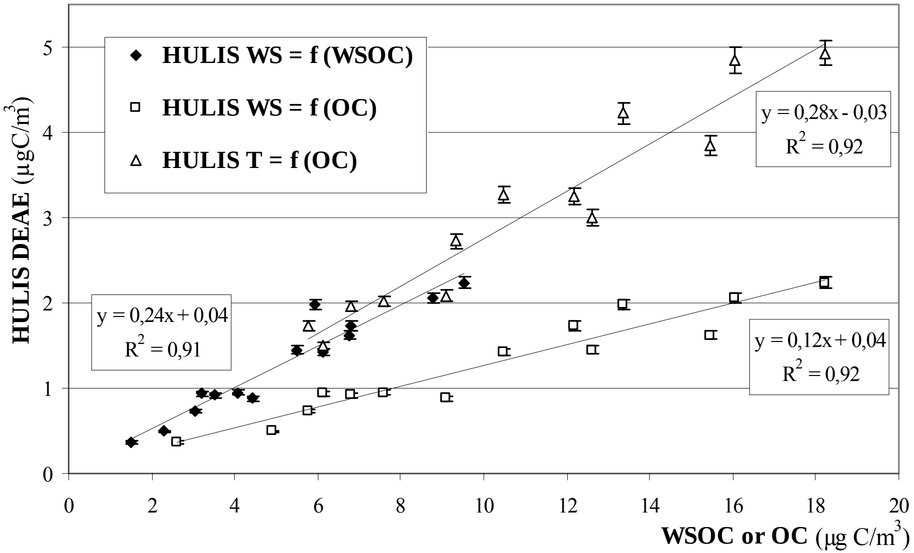

**Fig. 5.** Correlations between concentrations of WSOC, OC, and both HULIS extracts obtained with the DEAE protocol. Uncertainties include relative standard deviation of extraction efficiency determined with SRFA standard.

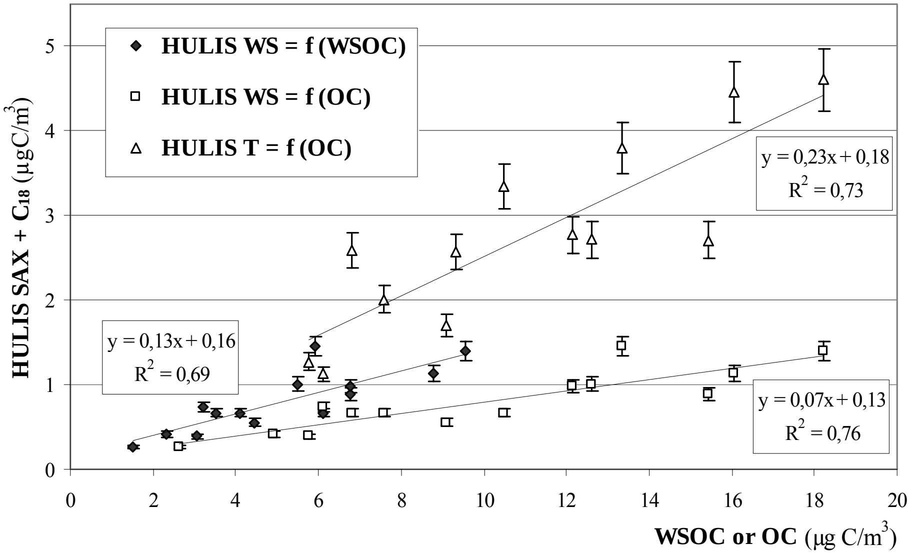

**Fig. 6.** Correlations between WSOC, OC, and HULIS extracted with the $C_{18}$+SAX protocol. Uncertainties include relative standard deviation of extraction efficiency determined with SRFA standard.