The water-soluble organic component of size-segregated aerosol, cloud water and wet depositions from Jeju Island during ACE-Asia

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Received 29 March 2004; received in revised form 23 September 2004; accepted 29 September 2004

Abstract

Water-soluble organic compounds (WSOC) in size-segregated aerosol samples, cloud water and wet depositions collected at Jeju Island during the ACE-Asia experiment were characterized in terms of main functional groups and chemical classes by means of liquid chromatography coupled with total organic carbon (TOC) analysis, and by nuclear magnetic resonance (NMR) spectroscopy. The surface-active character of the WSOC was also deduced by measuring the surface tension (ST) of cloud water, wet depositions and aerosol water-extracts as a function of WSOC concentration. WSOC in the size-segregated aerosol samples at the Kosan coastal site show the occurrence of oxidized species, enriched in the accumulation mode, and a functional group composition characteristic of continental industrialized areas, with a small impact from biomass burning sources. The chemical classes identified and quantified by liquid chromatography accounted for 88% of the water-soluble organic carbon on average. The relatively high proportion of polycarboxylic acids (PA, 33–40% of total characterized WSOC) observed throughout the campaign indicates the persistence of WSOC from continental pollution sources in air masses which spent up to 5 days in the marine boundary layer (MBL) of the Yellow Sea. The analysis of cloud water and wet depositions collected at a mountain site in Jeju shows substantial differences in the organic composition between the cloud/rainwater solutes and the water-soluble fraction of the aerosol at the coastal site, with PA acids contributing to cloud water WSOC in far smaller proportions (6–11%) than in the fine MBL aerosols. It was proposed that such differences resulted from the entrainment of aerosol particles from the lifted layers into the stratiform clouds. Following this hypothesis, the saturated aliphatic compounds determined by NMR analysis in the rainwater samples, which are also responsible for the observed significant ST lowering, were scavenged above the boundary layer and had possibly been transported from the continent in the lifted layers. The hypothesized features of the vertical profiles in the inorganic and organic aerosol chemical composition are in agreement with the results of aircraft-based measurements performed during the same experiment.

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Keywords: Water-soluble organic carbon; Atmospheric aerosols; Rainwater; NMR spectroscopy; Surface tension

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1. Introduction

ACE-Asia is the third in a series of experiments organized by the International Global Atmospheric Chemistry (IGAC) Project. The aerosol characterization experiments (ACEs) have been designed to improve knowledge of the effects of atmospheric aerosol on the Earth's climate system. ACE-Asia aims specifically to understand the properties of aerosols in the polluted atmosphere of Eastern Asia and the Northwest Pacific Ocean, and to assess their radiative forcing on climate (<http://saga.pmel.noaa.gov/aceasia/>). The agricultural and industrial activities in China, Korea and Japan are responsible for the high levels of pollution typically encountered in the region (e.g., [Zhang and Friedlander, 2000](#)). Furthermore, atmospheric pollutants are transported by westerly winds over the Yellow Sea, Sea of Japan and far into the North-Pacific region, with a consequent degradation of air quality in coastal and remote marine areas ([Arimoto et al., 1996](#)). The anthropogenic aerosols in the continental outflow typically consist of sulfate, organic matter and elemental carbon. Entrainments of mineral aerosol have also been observed, especially in late winter and spring, caused by aeolian dust storms occurring in the arid regions of China and Mongolia. Therefore, East Asian aerosol plumes comprise different layers of both natural and anthropogenic continental aerosols, which may eventually enter the marine boundary layer (MBL) and mix with sea salt particles ([Gao et al., 2003](#)).

In a companion paper ([Topping et al., 2004](#)), we have presented the results of an aerosol chemical characterization study performed at the Kosan site on Jeju Island, which is situated in the Yellow Sea, ca. 100 km south of the Korean peninsula. In particular, the size-segregated chemical characterization of the main inorganic and organic components of the MBL aerosols in Jeju was performed by chemical analysis on five-stage Berner impactor samples and by an aerodyne mass spectrometer (AMS). During the sampling period, air masses brought polluted continental aerosol from both China and Korea, carrying mainly sulfate and organic sub-micrometric particles. However, coarse aerosols consisting of sea salt and nitrate were also observed. Average air concentrations were lower when the air masses did not come directly from the continent, but spent 2–5 days over the Yellow Sea. The aerosol load decreased further, due to wet scavenging subsequent to the passage of two frontal systems on 24 and 28–29 April. Mineral dust was observed mixed with nss-sulfates and organic particles at the beginning of the sampling period (13 April) and after the first cold front, on 25–26 April. The two dust outbreaks originated from the northwestern and north-eastern deserts of China, and were associated with air masses which crossed polluted areas in China and Korea, respectively ([Huebert et al., 2003](#)).

Compared to the general aerosol characterization discussed in the first paper, the present study provides insight into the composition of the water-soluble organic carbon, resulting from an extensive organic chemical analysis of aerosol, cloud and wet deposition samples collected at Jeju. Water-soluble organic compounds (WSOC) have a potentially important role in aerosol–cloud interaction, as indicated by a number of studies which provide evidence that WSOC are contributors to cloud condensation nuclei (CCN) ([Novakov and Penner, 1993](#); [Cruz and Pandis, 1997](#); [Matsumoto et al., 1997](#)). The CCN ability of water-soluble organic particles have been explained by considering the effects of both the hygroscopic and surface-active properties of WSOC ([Shulman et al., 1996](#), [Facchini et al., 1999](#)), which in turn depends on the WSOC chemical composition. With regard to the East Asian environment, the chemical characterization of the water-soluble fraction of organic carbon highlighted the occurrence of oxidized species, mainly consisting of di-carboxylic acids and keto-acids, plus a few low-molecular-weight carbonyls (e.g. [Wang et al., 2002](#); [Yao et al., 2003](#); [Kawamura et al., 2003](#); [Mochida et al., 2003](#)). However, these studies have shown that the organic compounds identified account for only 2–8% of total WSOC. The application of spectroscopic techniques, namely proton nuclear magnetic resonance (^1H NMR), to aerosol and fog samples collected in an urban area in Japan have shown that the identified C_2 – C_9 carboxylic acids coexist with an unresolved mixture of compounds possibly accounted for by higher molecular weight species ([Suzuki et al., 1998, 2001](#)). Although such complex mixtures cannot be resolved at the molecular level, the determination of their average chemical structures and functional groups can be provided by the same ^1H NMR techniques on the basis of the chemical shift scale ([Decesari et al., 2000](#)). Data on functional group composition obtained by this approach are available, with respect to the East-Asian environment, only for one suburban site in Singapore ([Balasubramanian et al., 2003](#)). Finally, it should be noted that the application of spectroscopic techniques (such as ^1H NMR) is of special interest for modeling purposes, as it provides an average chemical composition which can be used to constrain the development of molecular models for WSOC ([Fuzzi et al., 2001](#)).

In the present study we employed recently developed spectroscopic and liquid chromatographic techniques ([Decesari et al., 2000](#)) for an in-depth chemical characterization of WSOC in size-segregated aerosol samples collected in the polluted MBL at Jeju, as well as in cloud and rain water sampled on a mountain site located on the same island. The surface tension (ST) of atmospheric water samples (cloud, wet depositions and aerosol extracts) was also measured to obtain original data on WSOC physical properties and their dependence on organic chemical composition.

2. Experimental section

2.1. Sampling of aerosol and wet deposition

Sampling was performed at two sites on Jeju Island, Korea, namely, Kosan and the 1100 m hill site (Fig. 1). The Kosan station ($33^{\circ}17'N$, $126^{\circ}10'E$) is located at the western edge of the island just on the cliff-top above the shoreline, while the 1100 m hill site ($33^{\circ}21'N$, $126^{\circ}27'E$) is on the slope of Halla Mountain at 1100 m altitude in the middle of a forest. Aerosol sampling was performed at Kosan by means of a five-stage Berner impactor. The cut-offs for each stage were: $<0.2\mu m$ (Backup filter); $0.2\text{--}0.5\mu m$ (stage 1); $0.5\text{--}1.5\mu m$ (stage 2); $1.5\text{--}5.5\mu m$ (stage 3); $5.5\text{--}10\mu m$ (stage 4). Stages 1 to 4 were equipped with tedlar substrates extensively pre-washed with milliQ water. The same cleaning procedure was adopted for the Teflon back-filters. Aerosol sampling lasted from 13 to 30 April, and a total of 35 size-segregated samples were collected. Eight diurnal samples were collected during the first part of the campaign (until 20 April), when air concentrations of aerosol were generally lower. The sampling time was then reduced to between 4 and 18 h during the last part of the experiment. Sampling of cloud water and wet depositions was performed at the 1100 m hill site on 23 and 28–30 April, when frontal systems passed over the Yellow Sea bringing stratiform clouds over Halla Mountain in two subsequent episodes. A Berner active collector operated during the first of the two cloud episodes. The system sampled cloud droplets in three size-segregated stages (I: $7\text{--}11\mu m$; II: $11\text{--}17\mu m$; III: $>17\mu m$) at a flow rate of $240\text{ m}^3\text{ h}^{-1}$. One active collector sample was obtained after 3 h sampling on 23 April, but the intermediate dimensional stage collected

an insufficient volume for chemical analysis and was therefore discarded. A stainless steel passive collector operated on 23 and 28 April, collecting mostly rain and drizzle during in-cloud conditions. Three wet deposition samples were collected on 23 April, and another nine on 28 April. Cloud water and wet depositions samples were stored in pre-washed Nalgene bottles, and kept frozen until analysis.

2.2. Chemical analysis of aerosol, cloud and wet deposition samples

Tedlar and Teflon substrates of the five-stage Berner impactor were extracted in deionized water in an ultrasonic bath. The aerosol water-extracts and cloud/rain water samples were then divided into aliquots for the different types of chemical determination: ion chromatography, total organic compounds (TOC) analysis, and organic speciation by ion-exchange chromatography and 1H NMR. Measurement of pH was also performed. Results of the ion chromatography and TOC of the Kosan aerosol samples are discussed by Topping et al. (2004).

The concentration of inorganic ions (NH_4^+ , Na^+ , K^+ , Ca^{2+} , Mg^{2+} , Cl^- , NO_3^- , SO_4^{2-}) was determined by ion chromatography (IC), by means of Dionex DX4500 and DX500 systems. The accuracy of IC measurements was better than 5%. The water-soluble organic carbon content of the samples was measured by a Shimadzu TOC-5000A liquid analyzer. The accuracy of TOC analysis ranges from 7% for 1 ppmC solution to 3% for concentrations higher than 2 ppmC.

The WSOC were characterized by the procedure proposed by Decesari et al. (2000), based on a combination of ion-exchange chromatography, func-

Fig. 1. Map of Jeju Island showing the locations of the two sampling stations. Underlying topography isolines are plotted every 200 m increments of altitude.

tional group investigation by proton nuclear magnetic resonance (^1H NMR) and TOC determination. Following this procedure, the WSOC mixture was separated by ion-exchange chromatography into three main classes of compounds: (a) neutral compounds (NC); (b) mono- and di-carboxylic acids (MDA); (c) polycarboxylic acids (PA). Fractionation into NC, MDA and PA was performed using a HPLC system (Hitachi L-7100) equipped with a DEAE-TSK gel column (7.5 mm i.d. $\times$ 7.5 cm), and a UV detector (Decesari et al., 2000). In addition, the water extracts of aerosol samples collected from 15 to 20 April were combined and fractionated at a preparative scale on a DEAE-cellulose gel column (Pharmacia), in order to obtain isolated WSOC fractions. This is a necessary step to obtain the HPLC calibration factors (Decesari et al., 2001). Combined extracts of backup filter + stages 1+2 and of stages 3+4 were fractionated separately, yielding specific calibration factors for fine and coarse aerosol, respectively. Accuracy of calibration was estimated on the basis of replicated preparative fractionations ($n=3$ and 2 for fine and coarse aerosol, respectively), turning out to be between 6% and 13% for the acidic classes (MDA and PA) and 25% for NC.

^1H NMR spectroscopy was adopted for the analysis of one individual size-segregated aerosol sample, collected on 13–14 April. The water extracts of the five stages of the sample were dried under vacuum and redissolved in D_2O solution. The ^1H NMR analysis was then performed in a 5 mm probe using a Varian Mercury 400. The same procedure was applied to four wet deposition samples collected on 23 and 28 April. Details on the experimental conditions can be found in Decesari et al. (2000, 2001).

2.3. Surface tension measurements

The aerosol extracts of the size-segregated aerosol sample collected on 13–14 April underwent to ST measurements at 25 °C temperature by means of SINTECH (Berlin, Germany) PAT1 tensiometer. The measurement was based on the axialsymmetric drop shape analysis (Loglio et al., 2001). First, a drop of sample was generated at the capillary tip, with a selected value of surface area. The sample was then left to stand for 30 min while the drop area was kept constant. At given time intervals, drop profiles were acquired and stored; subsequently, the value of ST was automatically calculated according to the Laplace equation. The ST lowering reported in Section 3.4 was estimated as the difference between the ST of pure water at 25 °C and the ST of the sample after 30 min of equilibration.

Cloud water and wet deposition samples underwent ST analysis under the same experimental conditions described above for aerosol extracts. Furthermore, aliquots of cloud and rainwater samples were evapo-

rated under vacuum in a step-wise procedure, decreasing the volume of liquid to a 1/20–1/100 of the original one. After each evaporation step, the ST was measured in order to obtain the dependence on solute concentration.

3. Results and discussion

3.1. Organic speciation of MBL aerosols

Fig. 2 shows the ^1H NMR spectra of the fine segregated sample collected on 13–14 April. The sample was collected at Kosan during an outflow of polluted air from northern China following the passage of a cold front on 11 April. In agreement with previous NMR analyses on atmospheric WSOC samples (Decesari et al., 2000; Graham et al., 2002), the spectra show a number of largely overlapping resonances, preventing any characterization at molecular level. The unresolved signals were integrated and attributed to principal functional groups on the basis of the main intervals of chemical shift (Fig. 3; Decesari et al., 2000).

Functional group analysis highlights the predominance of both saturated and unsaturated aliphatic moieties, with a minor contribution from hydroxylated aliphatics. Here the unsaturated aliphatic moieties are intended as methyls/methylenes/methynes bound to either $\text{C}=\text{C}$ (aromatic or vinylic substituents) or $\text{C}=\text{O}$ groups (carbonyls or carboxyls), the two categories being indistinguishable on the basis of the chemical shift alone. However, the low content of aromatic (Ar-H) and vinylic protons suggests that the hydrogen atoms characteristic of the unsaturated aliphatic groups are mainly in alpha position to carbonyls and carboxyls. It should be noted that due to the low signal-to-noise ratio of the spectra of the backup filter and of stage 4, the concentration of protons giving rise to broad bands (as in the case of aromatic protons) could be underestimated. The composition of WSOC remains fairly constant with aerosol size with the exception of the coarsest stage (Dp : 5.5–10 μm), whose WSOC exhibit a more saturated character. Conversely, WSOC on the other stages and on the backup filter, accounting for 91% of all water-soluble carbon, show large contributions from unsaturated structures. The ratio between aliphatic C-H groups bound to unsaturated carbon atoms and the C-H groups included in fully saturated structures varies from 1.0 to 1.3 from the backup filter to stage 2, and then decreases to 0.7 in the case of stage 4. Therefore, the higher WSOC air concentrations typically encountered in the accumulation mode size range (stages 1 and 2) are likely to be associated with compounds largely substituted by $\text{C}=\text{O}$ groups (carbonyls and carboxyls), i.e. more oxidized species.

Fig. 2. ^1H NMR spectra of the size-segregated aerosol sample collected at the Kosan site on 13–14 April. The horizontal axes show the chemical shift in ppm. The peak at 0 ppm corresponds to the internal standard (sodium 3-(trimethylsilyl)-2,2,3,3- d_4 -propionate (TSP d_4)). H-C: purely alkylic hydrogen atoms; H-C-C=: hydrogen atoms in alpha position to C=C or C=O groups; H-C-O: aliphatic C-H directly bound to an oxygen atom; H-Ar: aromatic hydrogen atoms. The signals at ca. 4.8 ppm (particularly evident in the stage 4 spectrum) are artefacts due to the suppression of the HDO peak. The spectrum of a field blank is also reported as a reference at the bottom of the figure.

The H-C-O moieties of alcohols and ethers account for only 7–13% of total non-exchangeable hydrogen atoms, and no distinct peaks of specific compounds (e.g., levoglucosan) could be found in this region of the spectra (Fig. 2). The finding is in agreement with the low concentrations of levoglucosan ($< 20 \text{ ng m}^{-3}$), estimated by sampling aboard a research ship on the Yellow Sea on 14 April (Mochida et al., 2003). The observed low content of hydroxylated groups does not

Fig. 3. Functional group composition of the size-segregated aerosol sample collected at Kosan on 13–14 April. H-C: purely alkylic hydrogen atoms; H-C-C=: hydrogen atoms in alpha position to C=C or C=O groups; H-C-O: aliphatic C-H directly bound to an oxygen atom; H-Ar: aromatic hydrogen atoms. The relative abundance of each functional group is estimated as the partial integrals of the spectra reported in Fig. 2.

support strong contributions from biomass burning sources, which have been characterized by NMR spectroscopy in rural Brazilian sites and Singapore (Graham et al., 2002; Balasubramanian et al., 2003). By contrast, the overall functional group budget of the 13–14 April sample matches the results of ^1H NMR analysis of fine aerosols collected in polluted industrialized areas in East Asia and Europe (Suzuki et al., 2001; Decesari et al., 2001). Therefore, the industrialized areas of northern China are the probable sources of the WSOC determined in the 13–14 April sample. The HPLC results for the samples collected in the 13–30 April period are summarized in Table 1, according to the classification of air masses presented by Topping et al. (2004). Average air concentrations of total WSOC and HPLC chemical classes were calculated for the n samples included in each sub-set of samples. Although the concentrations of HPLC classes could be determined in stages 1 and 2 for the majority of samples (23), the table only presents the data obtained from samples for which the full size-segregated composition was determined. A few samples showing a lack of data for stage 4 are also included, in order to improve the statistics for the other stages which account for 92–96% of WSOC.

The WSOC were separated by liquid chromatography on the basis of their retention factor on DEAE resins into (a) NC (not retained by the resin), (b) MDA (weakly retained) and (c) PA (strongly retained). All three classes were widely found in the Kosan aerosol samples, irrespective of the origin of the air masses. The sum of the HPLC fractions spans on average from 73% to 102% of total WSOC concentrations, depending on the dimensional stage (Fig. 4). The un-recovered fraction of water-soluble carbon may be due to the

Table 1

Average air concentrations and standard deviations (in parantheses) of total WSOC and WSOC fractions determined by HPLC analysis: NC (neutral compounds), MDA (mono-/di-acids) and PA (polyacids)

		WSOC	NC	MDA	PA
China: 13–15 April (<i>n</i> = 1)	Backup filter	0.25	0.04	0.09	0.09
	Stage 1	0.71	n.d.	0.18	0.14
	Stage 2	0.77	0.08	0.35	0.32
	Stage 3	0.33	0.07	0.28	0.07
	Stage 4	0.18	n.d.	0.06	0.01
Marine: 16–20 April (<i>n</i> = 3)	Backup filter	0.24 (0.06)	0.05 (0.00)	0.11 (0.06)	0.11 (0.04)
	Stage 1	0.63 (0.28)	0.10 (0.05)	0.25 (0.15)	0.25 (0.07)
	Stage 2	0.54 (0.10)	0.07 (0.03)	0.21 (0.07)	0.21 (0.04)
	Stage 3	0.18 (0.03)	0.04 (0.02)	0.09 (0.02)	0.09 (0.00)
	Stage 4	0.13	0.05	0.05 (0.03)	0.05
Korea 1: 21–23 April (<i>n</i> = 4)	Backup filter	0.55 (0.24)	0.08 (0.06)	0.36 (0.27)	0.27 (0.20)
	Stage 1	1.07 (0.17)	0.10 (0.01)	0.46 (0.05)	0.29 (0.04)
	Stage 2	0.81 (0.14)	0.08 (0.02)	0.32 (0.09)	0.19 (0.06)
	Stage 3	0.25 (0.03)	0.03 (0.01)	0.11 (0.01)	0.02 (0.01)
	Stage 4	0.11 (0.08)	0.02	0.03 (0.01)	0.01
Korea 2: 24–30 April (<i>n</i> = 10)	Backup filter	1.45 (1.01)	0.15 (0.12)	0.71 (0.57)	0.62 (0.48)
	Stage 1	1.41 (0.62)	0.13 (0.06)	0.61 (0.30)	0.50 (0.25)
	Stage 2	1.03 (0.45)	0.12 (0.05)	0.50 (0.29)	0.37 (0.20)
	Stage 3	0.39 (0.12)	0.07 (0.03)	0.26 (0.11)	0.07 (0.03)
	Stage 4	0.21 (0.15)	0.06 (0.05)	0.11 (0.07)	0.03 (0.02)

The impactor stages correspond to the following size intervals: $<0.2\mu\text{m}$ (backup filter), $0.2\text{--}0.5\mu\text{m}$ (stage 1), $0.5\text{--}1.5\mu\text{m}$ (stage 2), $1.5\text{--}5.5\mu\text{m}$ (stage 3), $5.5\text{--}10\mu\text{m}$ (stage 4). Concentrations in $\mu\text{g m}^{-3}$.

Fig. 4. Mean distribution of NC, MDA and PA in size-segregated aerosol samples collected at Kosan. The unresolved fraction was estimated as the difference between the total WSOC measured by TOC analysis and the sum of the three HPLC fractions. The mean distributions for each size interval were calculated by time-averaging the proportions obtained on the individual samples.

occurrence of volatile WSOC, which are not accounted for by the HPLC calibration (Decesari et al., 2001).

Concerning the relative proportions of HPLC classes, acidic classes dominate over NC, as observed in polluted continental environments during previous experiments

(Decesari et al., 2001). The NC fraction is systematically higher for stages 3 and 4 (coarse particles), whereas PA show a completely opposite behavior, accounting for 27–34% of total speciated WSOC in fine particles, but only 11–15% in the coarse mode. The low relative concentrations of NC in fine particles (11–15% on average) do not support a strong contribution from biomass burning processes, since biomass smoke WSOC contain more than 30% of NC, mainly in the form of anhydrosugars and phenols (Mayol-Bracero et al., 2002). The above result of the HPLC analysis is in agreement with the ^1H NMR features of the 13–14 April sample. The NC fraction is smaller during the highly polluted conditions on 13–15 April (Chinese outflow) and during the Korean outflows, compared to the marine period: $11 \pm 2\%$ and $19 \pm 3\%$ in the fine stages, for the polluted and marine cases, respectively. The average relative concentration of PA in the fine stages reached its maximum during the second Korean outflow ($40 \pm 2\%$ of total HPLC fractions), when the highest air concentrations of WSOC were also observed. In fact, relative concentrations of PA of 40% are typical of continental environments under severe polluted conditions (Decesari et al., 2001). It should be noted that the polyacidic fraction accounted for at least one third of total speciated water-soluble carbon in the fine stages

throughout the whole sampling period, and that the fraction observed during the marine regime ($33 \pm 4\%$) is not significantly lower than the one observed during the first Korean outflow ($34\% \pm 3\%$). This finding can be interpreted by hypothesizing one major (presumably continental) source of WSOC collected in the MBL at Kosan, with the organic aerosols undergoing only minor modifications during the permanence of air masses over the Yellow Sea. Indeed, the WSOC air concentrations in the period 16–20 April are only 50% lower than during the antecedent Chinese outflow and the following Korean one (21–23 April). In summary, the outcomes of HPLC analysis indicate the permanence of anthropogenic organic aerosols in the Yellow Sea MBL, following pollution outbreaks from China and Korea, which in turn originated from the extensive burning of fossil fuels. Therefore, WSOC from samples collected under ‘marine’ conditions have to be considered as ‘modified continental’, rather than genuine marine aerosol organic compounds (Lim et al., 2003).

3.2. General observations on chemical composition of cloud water and wet deposition samples

Table 2 provides a synopsis of the size-segregated cloud sample collected on 23 April and the rain samples collected on 23 and 28 April. The table also shows the concentrations of inorganic ions determined by IC and the WSOC obtained by TOC analysis. Solute concentration in cloud water is higher than in rainwater by a factor of 3 and 15 for dimensional stages 1 and 3, respectively. Sea salt accounts for the main part

(33–51%) of inorganic solutes in both cloud and rainwater samples on 23 April, although non-sea sulfates are equally important in rainwater composition on 28 April. The occurrence of sea salt in comparable relative amounts in cloud water and precipitation indicates that aerosol particles were lifted from the MBL and eventually entrained the stratiform clouds reaching the mountain station. For a direct comparison of cloud/rainwater solutes and their sources in the MBL, Table 3 reports the ionic composition of the simultaneous aerosol samples collected at the Kosan coastal site (Topping et al., 2004). It can be seen that the ratio between sea salt and nss-sulfate is higher in cloud/rainwater than in the aerosol, possibly due to the differences in scavenging efficiency of the two components. Cloud/rain samples and aerosol also differ in chemical composition with respect of the contributions of low-molecular weight organic acids and of calcium, which are both systematically higher in cloud/rainwater. Concerning acetic, formic and oxalic acids, the enrichment in cloud droplets via adsorption from the vapor phase has been invoked (Khare et al., 1999). Conversely, nss-calcium must be associated with crustal material, which is apparently not transported by MBL aerosol. High concentrations of calcium were observed in the aerosol phase at Kosan on 25–26 April, i.e. just after the passage of the frontal systems (Topping et al., 2004). The observation of an excess of calcium in cloud/rain samples with no correspondence to the MBL aerosol during the passage of the fronts indicates possible dust entrainments into clouds in the upper levels of the troposphere.

Table 2

Sample list, sampling times and ionic compositions of the cloud and wet deposition samples collected at the 1100 m Hill site

	Date	Time (BST)	pH	Na ⁺	NH ₄ ⁺	K ⁺	Mg ²⁺	Ca ²⁺	Formate	Acetate	MSA	Cl ⁻	NO ₃ ⁻	SO ₄ ⁻	Oxalate
<i>Active collector</i>															
BeC-I	23/04/01	16.30–19.23	5.61	9489	446	2697	933	4192	2357	4743	104	10,742	1906	5728	467
BeC-II	23/04/01	16.30–19.23													
BeC-III	23/04/01	16.30–19.23	6.68	38,945	6735	4520	5353	15,395	1658	1698	489	55,526	50,432	40,208	3,883
<i>Passive collector</i>															
SS1	23/04/01	16.15–18.25	4.84	3622	969	1895	469	2776	1260	772	< d.l.	3989	5073	6681	829
SS2	23/04/01	18.25–23.10	5.16	880	277	786	137	975	527	390	< d.l.	1184	1771	2547	248
SS4	23/04/01	23.30–10.10	6.01	1,164	219	555	212	970	66	118	< d.l.	1130	802	1285	326
SS6	28/04/01	04.35–05.00	6.06	791	655	562	176	1755	805	303	< d.l.	1310	2491	3570	452
SS7	28/04/01	05.00–05.30	4.76	284	419	217	63	686	431	355	< d.l.	377	614	1908	237
SS8	28/04/01	05.30–06.00	4.58	254	428	158	54	511	475	396	< d.l.	456	651	2739	237
SS9	28/04/01	06.00–06.15	4.71	133	241	110	35	349	391	283	< d.l.	202	350	1335	192
SS10	28/04/01	06.15–06.45	4.99	104	210	115	32	307	392	54	< d.l.	144	281	1,074	145
SS11	28/04/01	06.45–07.00	4.93	89	126	109	22	229	319	261	< d.l.	123	209	750	150
SS12	28/04/01	07.00–07.30	4.84	84	78	116	18	175	66	49	< d.l.	144	329	511	120
SS13	28/04/01	07.30–09.45	4.83	133	53	151	23	270	137	180	< d.l.	235	244	421	144
SS14	28/04/01	09.45–11.20	5.06	79	44	116	22	210	244	170	< d.l.	105	152	295	92

The concentrations of ionic species (except for H⁺) are expressed in ppb.

Table 3

Ionic composition (as % equivalents) of cloud water samples and wet depositions collected at the 1100 m hill station, and of the aerosol samples (K-23Apr, K-28Apr) collected simultaneously at the Kosan coastal site

	H (%)	Na (%)	NH ₄ (%)	K (%)	Mg (%)	Ca (%)	Acetate (%)	Formate (%)	MSA (%)	Cl (%)	NO ₃ (%)	SO ₄ (%)	Oxalate (%)
BeC-I	0	30	2	5	6	15	6	4	0	22	2	9	1
BeC-III	0	25	6	2	7	11	0	1	0	23	12	12	1
SS-23Apr	1	19	6	6	6	19	1	2	0	13	8	15	3
SS-28Apr	11	7	9	4	3	19	3	6	0	8	7	20	4
K-23Apr	3	11	29	2	2	4	1	1	0	6	13	25	2
K-28Apr	4	8	33	2	1	4	1	1	0	6	4	35	1

BeC-I and -III refer to the first and third dimensional stages of the active collector for cloud water. SS-Apr23 and SS-Apr28 are volume-averaged wet deposition samples collected on 23 and 28 April, respectively.

3.3. WSOC composition of cloud water and wet deposition samples

The ¹H NMR spectra were obtained for wet deposition samples collected at the beginning of precipitation events on 23 and 28 April. The spectra show large overlaps of resonances, whose envelopes were integrated and attributed to a few major functionalities (Fig. 5). The functional group analysis indicates that aliphatic structures highly saturated and substituted with hydroxyl groups represent the dominant moieties in these samples (Fig. 6). The spectra show some resemblance to those of fatty acids, with peaks at 1.3 and 0.9 ppm of chemical shift, attributable to abundant methylenic chains with terminal methyls, and a distinct peak at 1.6 ppm possibly due to methylenes in β position to carbonyls. The ¹H NMR features of the wet deposition samples are evidently very different from those of the aerosol sample collected at Kosan (Fig. 2), whose saturated moieties are much less concentrated and consist mostly of short chains and rings with a few terminal methyls.

The HPLC classes (NC, MDA, PA) contributed significantly to the WSOC of cloud water and wet depositions, accounting for 42–80% and 95–98%, respectively (Table 4). The un-recovered fraction can be attributed to volatile substances, such as formaldehyde and mono-carboxylic acids C₁–C₂, which are partly lost during the HPLC calibration procedure. Indeed, acetic acid, formic acid and oxalic acid determined by IC accounted for 4–16% of the dissolved carbon concentration. The WSOC composition determined by HPLC is characterized by a high proportion of acidic compounds (70–85% of speciated WSOC), which are mostly MDA whereas PA contributed to a much lesser extent (6–11% of speciated WSOC). These findings can be compared with the HPLC compositions determined for the aerosol at the Kosan site during the second part of the campaign when the frontal systems passed over Jeju

(‘Korean 1 and 2’ cases in Table 1). It can be seen that the small fraction of PA characteristic of the cloud/rainwater samples is also found in the aerosol only in the coarse size range (13–16% of speciated WSOC). In contrast, the WSOC in the accumulation mode aerosol exhibit a polyacidic fraction of 31% and 38% in the periods 21–23 April and 24–30 April, respectively, in agreement with the average composition observed during the whole duration of the campaign (see Section 3.1). The overall set of HPLC measurements indicates that the WSOC composition of cloud/rainwater samples can be reconciled with that of the fine aerosol particles under none of the four regimes characteristic of the MBL and considered in this study. The observed difference in WSOC composition between cloud/rainwater and MBL aerosol can be partly attributed to a higher scavenging efficiency of the coarse aerosol mass compared to that of the fine fraction. However coarse particles ($D_p > 1.5 \mu\text{m}$) account for only 13% of the total WSOC mass on average in the period 24–30 April, and for 17% in the whole campaign. An alternative explanation is that the clouds at the 1100 hill site scavenged aerosol particles exogenous to the MBL, thus pointing to the same conclusions as the IC analysis, suggesting that the sea salt particles were lifted to the elevation of stratiform clouds and mixed (either before or in-cloud) with pre-existing particles of continental origin. Following this interpretation, the original features of the WSOC functional group composition determined by ¹H NMR in the wet deposition samples can be attributed to organic compounds scavenged above the boundary layer; such compounds consist of saturated aliphatic carboxylic acids which could not form by secondary processes in the atmosphere, and possibly originated from distant continental primary sources.

Aircraft measurements performed during the ACE-Asia experiment above the Yellow Sea and Sea of Japan showed that OC and sulfate were highly stratified in the

Fig. 5. ^1H NMR spectra of wet deposition samples collected on 23 and 28 April. The horizontal axes show the chemical shift in ppm. The peak at 0 ppm corresponds to the internal standard (sodium 3-(trimethylsilyl)-2,2,3,3- d_4 -propionate (TSP d_4)). H-C: purely alkylic hydrogen atoms; H-C-C=: hydrogen atoms in alpha position to C=C or C=O groups; H-C-O: aliphatic C-H directly bound to an oxygen atom; H-Ar: aromatic hydrogen atoms. The band between 4.0 and 4.5 ppm in the spectra of samples SS1 and SS7 is an artefact due to the suppression of the HDO peak.

troposphere (Bahreini et al., 2003, Maria et al., 2003). In particular, a maximum in the vertical profile of aerosol OC was observed at ca. 800 m altitude and approximately 200 km ENE to Jeju on 27 April, i.e. just before the passage of the frontal system (and the following dust event). The lifted aerosol layer was substantially heterogeneous to the MBL aerosol, and was characterized by a higher ratio between OC and sulfates. The same paper also presents the characterization of organic particles in the upper layer, provided by an AMS, which showed a very low content of C=C bonds (aryl and vinyl groups), compared to saturated aliphatic moieties.

Fig. 6. Functional group composition of wet deposition samples collected on 23 and 28 April. H-C: purely alkylic hydrogen atoms; H-C-C=: hydrogen atoms in alpha position to C=C or C=O groups; H-C-O: aliphatic C-H directly bound to an oxygen atom; H-Ar: aromatic hydrogen atoms. The relative abundance of each functional group is estimated as the partial integrals of the spectra reported in Fig. 5. Total organic hydrogen concentrations in the four samples were 0.67, 0.27, 0.40 and 0.16 mmolHL $^{-1}$ respectively for SS1-23Apr, SS2-23Apr, SS6-28Apr, SS7-28Apr.

Table 4

Concentrations of total WSOC, C1–C2 acids from ion chromatography, and of HPLC classes (NC: neutral compounds; MDA: mono-/di-acids; PA: polyacids) of cloud and wet deposition samples

	WSOC	C1–C2 acids	NC	MDA	PA
<i>Active collector</i>					
BeC-I	17.2	1.7	4.3	8.7	0.9
BeC-II	—	—	—	—	—
BeC-III	51.7	1.8	3.6	15.5	2.4
<i>Passive collector</i>					
SS1	9.3	0.7	1.7	5.6	0.9
SS2	3.2	0.3	0.5	2.6	0.2
SS4	4.8	0.1	—	—	—
SS6	5.1	0.4	1.0	2.7	0.5
SS7	2.5	0.3	0.4	2.0	0.3
SS8	2.1	0.3	0.0	1.9	0.2
SS9	1.4	0.2	0.3	1.2	0.2
SS10	1.2	0.2	0.2	0.8	0.1
SS11	1.1	0.2	0.2	0.7	0.1
SS12	0.8	0.1	0.2	0.6	0.1
SS13	1.2	0.1	0.3	1.0	0.1
SS14	1.1	0.1	0.0	0.7	0.1

All concentrations are expressed as ppmC. BeC-I and -III refer to the first and third dimensional stages of the active collector for cloud water.

It is worth noting that the results from the AMS match the functional group composition derived by ^1H NMR on wet deposition samples at the 1100 m hill site (Fig. 6). The overall set of aircraft measurements (Chin et al.,

2003; Bahreini et al., 2003; Mader et al., 2003, Maria et al., 2003) showed that layers of polluted (and OC rich) aerosols in the middle troposphere were quite common throughout the campaign, either mixed or unmixed with layers of dust particles which originated, conversely, from the arid areas of Mongolia and China (Lim et al., 2003; Zhang et al., 2003).

Table 5
ST of cloud water (BeC-I and -III) and wet deposition samples

	WSOC (ppmC)	Surface tension (mNm ⁻¹)
BeC-I	17.2	71.0
BeC-III	51.7	64.4
SS1-23Apr	9.25	68.0
SS2-23Apr	3.15	70.8
SS6-28Apr	5.07	70.7
SS7-28Apr	2.53	71.3

The total dissolved WSOC content is also reported.

Fig. 7. ST lowering versus total WSOC concentration ("TOC" as ppmC) for the size-segregated aerosol sample collected on 13–14 April and for cloud water (BeC-I and -III) and wet deposition samples (SS) collected on 23 and 28 April. In the case of the BeC-I sample and SS samples, each curve collects the measurement performed on the original sample (the point in each curve at the lowest TOC concentration) and those performed on aliquots concentrated in laboratory according to the procedure described in the text.

3.4. Surface tension of aerosol, cloud and wet depositions

Table 5 reports the ST lowering of cloud and wet deposition samples collected at the 1100 m hill site. The ST lowering of each cloud/rainwater sample is also plotted in Fig. 7 versus dissolved water-soluble carbon ("TOC") for the aliquots of samples concentrated according to the procedure described in Section 2.3. The ST lowering of the water extracts of the five-dimensional stages of the aerosol sample collected on 13–14 April is reported in the same figure. The figure reveals a clear dependence of ST lowering on WSOC concentration in all samples, but also a large variability among samples. The aerosol extracts show very limited ST lowering, whereas the ST of rainwater significantly differs from that of pure water also at dissolved WSOC concentration of 10 ppmC. These are by far the most pronounced ST lowerings ever observed in atmospheric water samples (including cloud/rain and aerosol extracts) (Facchini et al., 2000). The rheological properties of the surface films forming on wet deposition samples at the 1100 m hill station were discussed in the paper by Decesari et al. (2003), where they were linked to the solubility properties of the film-forming compounds. These measurements showed that the elasticity of the films on Jeju rainwater samples is less than that of completely insoluble fatty acids (like stearic acid) but higher than that of standards of natural high-molecular weight carboxylic acids, like the Suwannee River fulvic acid (water solubility: ca. 1/100 g H₂O), indicating that the compounds responsible for the formation of the films on Jeju rain samples are slightly soluble in water (< 1/100 g H₂O). This finding is in agreement with the chemical characterization provided by ¹H NMR, which highlighted the occurrence of abundant saturated aliphatic moieties responsible for the partial hydrophobic character of WSOC (see previous section). WSOC extracted from aerosol/fog in continental polluted environments are characterized by more oxidized structures with abundant C=C and C=O groups (Decesari et al., 2000) as in the case of Kosan aerosols, and typically form less elastic films (Decesari et al. 2003) and are also less efficient as surfactants.

4. Conclusions

Size-segregated aerosol samples were collected at a coastal site (Kosan) on Jeju Island, Korea, from 13 to 30 April during the ACE-Asia experiment, and were subsequently analyzed for their organic chemical composition by means of HPLC-UV and ¹H NMR techniques. In addition, cloud water and wet deposition samples were collected at a mountain site (1100 m hill) on 23 and 28 April, during the passage of two frontal systems over Jeju. Cloud and rain water samples underwent the same analytical protocol as the aerosol

extracts. The WSOC extracted from the Kosan aerosol samples show the occurrence of extensively oxidized species with a lower amount of residual saturated aliphatic moieties and a few hydroxylated substances. Around 85% of WSOC in fine fraction are recovered into NC, MDA and PA. Acidic compounds are more abundant than NC in all aerosol size intervals, and the percentage of PA among total acidic classes varies from 15% on the coarse stages to 43% in the fine fraction. This WSOC chemical composition has been related to the either primary and secondary products of fossil fuel combustion in China and Korea. The minor changes in the organic composition observed during the transitions between polluted and marine regimes indicates the persistence of pollutants in the boundary layer of marine coastal areas. Stratiform clouds passing over Jeju on 23 and 28 April scavenged aerosols from the MBL, incorporating sea salt and sulfate into cloud droplets and raindrops. However, the occurrence of calcium and of carboxylic acids with aliphatic straight chains in the cloud/rain samples collected at the mountain site can be related to additional sources of cloud water solutes in the upper-level aerosol layers. The observed differences in chemical composition between the aerosols at Kosan and the cloud/rainwater at the 1100 m hill site are in agreement with the data collected by aircraft measurements during the ACE-Asia experiment, which showed a vertical profile of aerosol chemical composition also in the first 1000 m of altitude (Bahreini et al., 2003). Our data indicate that aliphatic carboxylic acids transported in the lifted layers are scavenged in cloud and are found in cloud/rain samples. Their occurrence in rainwater was found to be responsible for the significant degree of ST lowering (from 4 to 10 mNm⁻¹ for TOC = 10 ppmC). Such lowering was not observed in the MBL aerosol extracts, suggesting that the aerosol surface-active agents were highly stratified over Jeju during the ACE-Asia campaign. Due to the known effect of ST changes on the nucleation of cloud droplets (Facchini et al., 1999), the occurrence of highly surface-active WSOC in lifted aerosol layers cannot be neglected in modeling aerosol/cloud interaction processes.

Acknowledgements

Funding for this work was provided by the UK Natural Environment Research Council under grant numbers NER/A/S/2000/00442 and GR3/12499. This paper is a contribution to the International Global Atmospheric (IGAC) Project.

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