

The Solubility Characteristics of Organic Compounds in Urban Aerosol Samples

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Abstract

The solubility characteristics of organic compounds were studied in terms of the extraction efficiency as a function of the polarity of the organic solvent, and the acidity of water in urban aerosol samples collected in University of East Anglia (UEA), Norwich, England. The extraction efficiency of organic compounds were evaluated with respect to the organic carbon, -nitrogen and -hydrogen by means of a wide range of solvent which include polar and nonpolar organic solvents as well as acids and alkaline water. In addition, after being dissolved in aqueous solution, the aqueous chemistry of organic compounds were studied in terms of the organic metal complexes in aerosol, which were studied with oxalic acid, copper, and zinc. The results of this study indicate that solubility characteristics of organic compounds depend on the polarity of the solvents and the acidity of the solvents. In particular, some organic compounds are water soluble, even though they are much smaller than acetone soluble fractions. In the comparison between polar organic solvent extraction and non-polar organic solvent extraction, it can be thought that significant fraction of organic compounds analysed in the aerosol samples, are polar organic compounds because of the higher extraction efficiencies of organic compounds in polar organic solvent extraction than in nonpolar organic solvent extraction. Regarding the study of the oxalic-metal complexes, it can be thought that most oxalic acids are present in the form of oxalic-copper complexes in the aerosols collected at UEA.

Key words : Urban Aerosol, Polarity, Acidity, Extraction efficiency, Oxalic-metal complexes

1. INTRODUCTION

Organic compounds are a significant fraction of the urban aerosol and have now become relevant to policy making together with concerns over the direct toxic effect of some specific organic compounds (Preston *et al.*, 1996). They can be affected the meteorological condition through the formation of cloud by acting as condensation nuclei. Novakov and Penner (1993) suggested that organic aerosols may play at least as important as sulphate aerosols in determining the climate

effect of clouds in regions that are affected by anthropogenic pollutants. However, in recent years, the importance of organic compounds are not only based on the direct toxic effect and the condensation nuclei for the formation of cloud, but also based on the aqueous chemistry connected with mostly trace metals. In aqueous solution, the dissolved organic compounds can complex with trace metals and can affect metal aquatic biogeochemical cycles. In particular, the changing trace metal separation by organic metal complexes in hydrological cycles can affect biological uptake, bioto-

xicity, adsorption/desorption reactions and precipitation/dissolution reactions. So far, the source of organic ligands complexing with the dissolved trace metals has previously been assumed to originate from terrestrial run off or in situ biological regeneration and/or production in water column or from the sediment. However, in recent year, the dissolved organic metal complexing ligands have been detected in rain waters (Nimmo & Chester, 1993). These results indicated that atmospheric wet deposition might be a significant additional source for the dissolved organic metal complexing ligands, which showed the importance of organic compounds in aerosol.

Several studies have been carried out for organic compounds from urban aerosols, and have been indicated the importance of solubility characteristics of organic compounds in terms of the environmental impact of organic compounds (Gundel & Novakov, 1984; Daisey *et al.*, 1982; Grojean, 1975). In particular, the solubility characteristics of organic compounds can vary to the aqueous chemistry of the dissolved organic compounds in aqueous solution. For example, the solubility characteristics of organic compounds are the key factor to determining the contribution of organic compounds as the dissolved organic metal ligands. Solubility characteristics of organic compounds have been studied by the extraction of organic compounds using polar and/or nonpolar organic solutions, which is mainly connected with the analysis of organic compounds in a laboratory. The analysis of organic compounds is the most fundamental process for the control of organic compounds in aerosol. In this case, polar and nonpolar organic solvents which were divided by the polarity, have been mostly used. In general, the extraction process of organic compound has been performed by the nonpolar organic solvents such as benzene, ether, hexane or cyclohexane, since polar organic solvents such as acetone can extract inorganics as well as organics, even though some studies reported that extraction efficiencies of organic compounds are much higher in the polar organic solvents than in the nonpolar organic solvents.

In contrast, the importance of solubility characteristics of organic compounds is not only based on the analysis of organic compounds but also based on that whether the organic compounds are hydrophobic or hydrophilic. Whilst the solubility characteristics of organic compounds for the polarity of solvents is connected with the analysis of organic compounds in a laboratory, the solubility characteristics of organic compounds for water is connected with the environmental behavior of organic compounds considering that the most dominant solvent in the atmosphere is water. For example, in the aerosol model suggested by Graedel and Weschler (1981), the model particle consists of an insoluble core and this core is surrounded by a layer of water which may account for 30% or more of the particles weight, depending on the relative humidity. Therefore it was reported that this layer which contains significant amount of dissolved inorganic and organic compounds can affect the surface properties of aerosol particles through the composition of the surface layer (Graedel & Wescher, 1981). In the composition of the surface layer, it is covered by a surface film of organic material consisting of polar molecules such as fatty acids, alcohol's etc. with their polar functional groups oriented towards the liquid core. The nonpolar part made up by an aliphatic chain of C- and H-atoms is oriented towards the surface. Therefore the solubility characteristics of organic compounds for water is the key factor to determining the composition of surface layer of aerosol which would influence the sticking probability of gaseous molecules to the surface of the aerosol.

The importance of solubility characteristics of organic compounds for water also can be shown by Saxena *et al.* (1995). They suggested that organic compounds can affect hygroscopic behavior of atmospheric particles by the hydrophilic or the hydrophobic fractions of organic compounds in the atmospheric particles. A hydrophobic fraction of organic compounds such as high-molecular weight alkanes, alkanic acids, alkenic acids, aldehydes and ketons, can exhibit soaplike surfactant behavior, which are unlikely to

absorb water. In fact, the film may act as a barrier to transfer water across the particle surface and thus prevent water absorption by hydrophobic fractions of organic compounds in the particle (Gill *et al.*, 1983). In contrast, a hydrophilic fraction of organic compounds in particles such as lower-molecular weight carboxylic acids and dicarboxylic acids are likely to adsorb water. Therefore the fractions of hydrophobic or hydrophilic organic compounds in the atmospheric particles can affect the water content of atmospheric particles which is one of the important factors governing the total mass concentration of air borne particles, their acidity, the amount of light they scatter, their aqueous phase chemical reaction rates, and their ability to act as cloud condensation nuclei (CCN).

However, these solubility characteristics of organic compounds for water have not been fully understood so far. In particular, the study for the solvent characteristics of water in the atmosphere can vary with acidity, the effect of water acidity has been neglected in terms of the solubility characteristics of organic compounds, whilst the effect of the polarity of organic solvents on the extraction efficiencies or organic materials has been studied before. In this study, the solubility characteristics of organic compounds were evaluated with respect to the extraction efficiency of organic carbon, organic nitrogen and organic hydrogen as a function of the polarity of the organic solvents and the acidity of water. In addition, the organic-metal complexes were estimated to study the aqueous chemistry of organic compound after being dissolved in aqueous solution and studied with regard to Zn^{2+} , Cu^{2+} and oxalic acid.

2. MATERIALS AND METHODS

The aims of this experiment are : firstly, to evaluate the extraction efficiency of organic compounds as a function of the polarity and the acidity of solvents; secondly, to analyze the oxalic acid and trace metals such as Cu^{2+} , Fe^{2+} , and Zn^{2+} . In these trace metals analyzed in this study, concentration levels of Cu^{2+}

and Zn^{2+} were used as the total concentrations Cu^{2+} and Zn^{2+} of for the estimation of oxalic-metal complexes in aerosol. The extraction efficiency of organic compounds from urban aerosol sample were evaluated in terms of organic carbon, organic nitrogen and organic hydrogen. Also NH_4^+ and NO_3^- were analyzed for the substitution of inorganic nitrogen, because it was reported that the polar solvent such as acetone and water can extract not only the organic compounds but also the inorganic compounds which are thought to mostly NH_4^+ and NO_3^- (Saxena and Hildermann, 1996). Therefore, in this study, organic carbon, organic nitrogen, organic hydrogen, NH_4^+ , NO_3^- , oxalic acid and trace metals such as Cu^{2+} , Fe^{2+} , and Zn^{2+} were analyzed.

2.1 Sample preparation

The aerosols were collected at the University of East Anglia which is located near Norwich city centre in UK in June, 1997. Before solvent extraction, the aero-

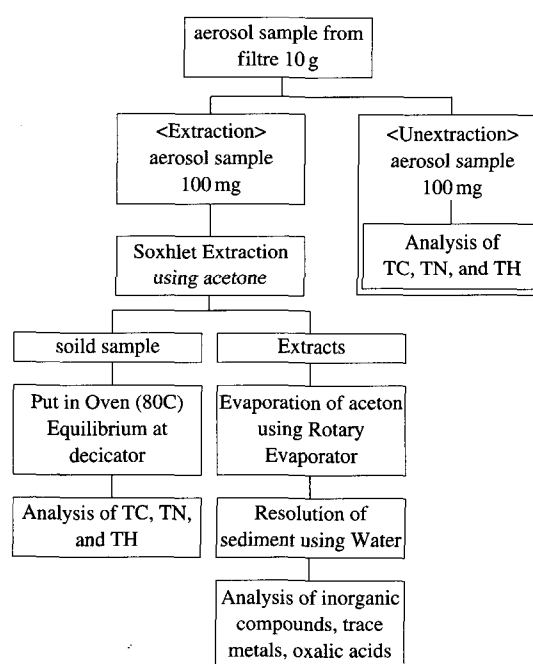


Fig. 1. The experimental procedure used in this study.

sols which have the diameter of more than 250 μm were eliminated using a sieve, also the aerosols were mixed through shaking for 30 mins. After these preparations, each 100 mg of aerosol sample was prepared for the solvent extractions. All aerosol samples prepared in this study were exposed in the desiccator which was prepared for the HCl fumigation overnight. This step was carried out to eliminate the contribution of inorganic carbon from aerosol samples by the reaction between HCl and inorganic carbons. Fig. 1 showed the summary of this experimental procedure.

2. 2 Solvent extraction

In order to evaluate the extraction efficiency of organic compounds with the polarity of solvents, with each, 50 mL of *n*-hexane and 50 mL of acetone were used. In this extraction process, aerosol samples were extracted individual solvents as well as 50 mL of the binary mixtures which is the 50% volume of *n*-hexane and 50% volume of acetone, and the successive extraction which is carried out by acetone (50 mL) extraction after *n*-hexane (50 mL) extraction. All solvent extractions were carried out using soxhlet extractors during 6 hours. In order to evaluate the extraction efficiency of organic compounds with the acidity of solvents, the acidified water (50 mL) of pH 2.5, the water (50 mL) of pH 6.0, and the alkaline water (50 mL) of pH 11.0 were used. These extraction process were carried out through shaking during 4 hours.

2. 3 Analysis

Organic carbon, organic nitrogen and organic hydrogen: As shown in Fig. 1, organic carbon, organic nitrogen and organic hydrogen were analyzed from sediments of aerosol sample produced from solvent extraction using the elemental analyzer (EA 1108, Carlo ERBA Instrument, USA). The sulphanilamide (Carbon: 41.85%, Nitrogen: 16.26%, Hydrogen: 4.68%, Elemental Microanalysis Limited) was used as the standard material for the analysis of organic carbon, organic nitrogen and organic hydrogen. For this analysis, aerosol samples were dried at the temperature of

80°C in an overnight, to eliminate the effect of organic solvents. The amount of standard materials and aerosols used for the analysis of these compounds using an elemental analyzer are approximately 3 mg and 5 mg, respectively.

NH₄⁺ and NO₃⁻: The NH₄⁺ and NO₃⁻ were analyzed in extracts produced from solvent extractions of aerosol samples, using the selective electrode method. In this study, BDH ion selective electrodes which attached with the reference electrode was used to analyze NH₄⁺ and NO₃⁻. In addition, NH₄Cl and KNO₃ were used as the standard materials for the analysis of NH₄⁺ and NO₃⁻, respectively. For the analysis of these compounds, extracts which were produced from the organic solvents extraction, were evaporated using the rotary evaporator and then the residues were redissolved by water.

Cu²⁺, Fe²⁺, and Zn²⁺: These trace metals were analyzed in extracts produced from solvent extractions of aerosol samples using the atomic absorption spectrometer (SpectrAA-10, Varian). In this study, all sample solutions used for the analysis of trace metals were same with that used for the analysis of NH₄⁺ and NO₃⁻.

Oxalic acid: Oxalic acid was analyzed in extracts produced from solvent extractions of aerosol samples using ion-chromatograph (Dionex 4000I, Dionex Ltd.). For the separation of oxalic acid, AS12A column (Dionex Ltd.) attached with guard column (AG 12A, Dionex Ltd.) was used. The eluents used were sodium hydroxide (strong preferential binding to the column) and water (weak preferential binding). The standard material which had the maximum limits of impurities of not less than 99.5% of purity was used in this study.

3. RESULTS AND DISCUSSION

3. 1 Extraction efficiencies (E.F.) of organic carbon, -nitrogen and -hydrogen

The solubility characteristics of organic compounds from urban aerosol samples were evaluated in terms of the E.F. of organic carbon, -nitrogen and -hydrogen

as a function of the polarity and the acidity of solvents. Table 1 showed E.F. of organic carbon, -nitrogen and -hydrogen evaluated with various solvents in this study. E.F. were calculated using the ratio of each organic compound analysed in the unextracted aerosol sample and in the extracted aerosol sample which was shown in experimental procedure of Fig. 1. For example, the E.F. of organic carbon (O.C.) was calculated as follows:

$$\text{E.F.} = \frac{\text{O.C. in unextracted aerosol sample} - \text{O.C. in extracted aerosol sample}}{\text{O.C. in unextracted aerosol sample}} \times 100$$

5 mg of aerosol sample was used to analyze organic carbon, -nitrogen and -hydrogen using an elemental analyzer. Therefore, in order to calculate the E.F. of each organic compound, the analytical results from the elemental analyzer, which is based on the 5 mg of aerosol sample, were converted using the amount of aerosol sample which decreased after solvents extractions with E.F. of organic compounds.

E.F. with the polarity of solvent: In this study, in order to evaluate the solubility characteristics of organic compounds for the polarity of solvents, E.F. of organic carbon, -nitrogen, and -hydrogen were evaluated for acetone, n-hexane, the binary mixtures of 50% volume of acetone and 50% volume of n-hexane, and successive extraction using acetone after n-hexane extraction. Fig. 2 shows E.F. of organic carbon, -nitrogen and -hydrogen with these organic solvents. E.F. of organic carbon and organic hydrogen have the highest acetone E.F. than in other organic solvents. However, the E.F. of organic nitrogen is the highest in the binary mixture than in other solvents. In comparison of E.F. of organic carbon, -nitrogen and -hydrogen between the polar organic solvent and the nonpolar organic solvent, E.F. of organic compounds studies in this study are much higher in polar organic solvent than in non-polar organic solvent. Also in the comparison between non-polar organic solvent extraction and other solvent extraction such as the binary mixture extraction and successive extraction, E.F. of organic compounds analyzed in this study, are much higher in the binary mixture extraction and in the successive extraction than in the non-polar organic solvent extraction. In the comparison between the binary mixture extraction and the successive extraction, E.F. of organic compounds are slightly higher in the binary mixture than in the successive extraction. The order of E.F. for organic compounds is shown as below:

Table 1. The summary of extraction efficiencies of organic compounds with various solvents in this study.

Solvents	Aerosol sample	Organic Carbon				Organic Nitrogen				Organic Hydrogen			
	Amount	CH & N (5 mg)		Aerosol sample		CH & N (5 mg)		Aerosol sample		CH & N (5 mg)		Aerosol sample	
	(mg)	C(mg) ⁽¹⁾	C(%)	C(mg)	E.F.(%)	N(mg)	N(%)	N(mg)	E.F.(%)	H(mg)	H(%)	H(mg)	E.F.(%)
Unextracted A ⁽⁵⁾	100	0.96	19.1 ⁽²⁾	19.10		0.19	3.7	3.70		0.17	3.3	3.30	
Water (pH 6.0)	72	1.29	25.8	18.57 ⁽³⁾	2.74 ⁽⁴⁾	0.14	2.7	2.48*	32.97	0.19	3.7	2.66	19.27
Acid (pH 2.5)	72	1.30	26.0	18.72	1.99	0.13	2.6	2.65*	28.38	0.18	3.5	2.52	23.64
Alkaline (pH 11.5)	70	1.60	21.1	14.77	22.67	0.10	1.9	1.87*	49.46	0.15	3.0	2.10	36.36
n-Hexane	87	0.92	18.3	15.92	16.64	0.12	2.3	2.00	45.92	0.17	3.4	2.96	10.36
Acetone	66	0.81	16.2	10.69	44.02	0.11	2.1	1.70*	54.50	0.15	3.0	1.98	40.00
Binary Mixture	71	0.83	16.6	11.79	38.29	0.11	2.1	1.49	59.70	0.14	2.8	1.99	39.76
S.E. ⁽⁶⁾	78	0.82	16.4	12.79	33.03	0.10	2.0	1.56	57.84	0.17	3.3	2.57	22.00

Note: (1) The analytical result of CH & N analysis using 5 mg of aerosol sample.

(2) 19.1% = (0.96 mg / 5 mg) × 100; 5 mg is amount of aerosol sample used for the analysis of CH & N by an elemental analyzer.

(3) 18.57 mg = (1.29 mg × 72 mg) / 5 mg; 72 mg is the amount of aerosol sample after being extracted by water.

(4) 2.74% = [(19.1 mg - 18.58 mg) / 19.1 mg] × 100; 19.1 mg is the amount of organic carbon analysed from the unextracted aerosol sample.

(5) Unextracted aerosol sample.

(6) Successive extraction.

(*) The amount of inorganic nitrogen was substituted from total nitrogen amount to calculate the extraction efficiency of organic nitrogen.

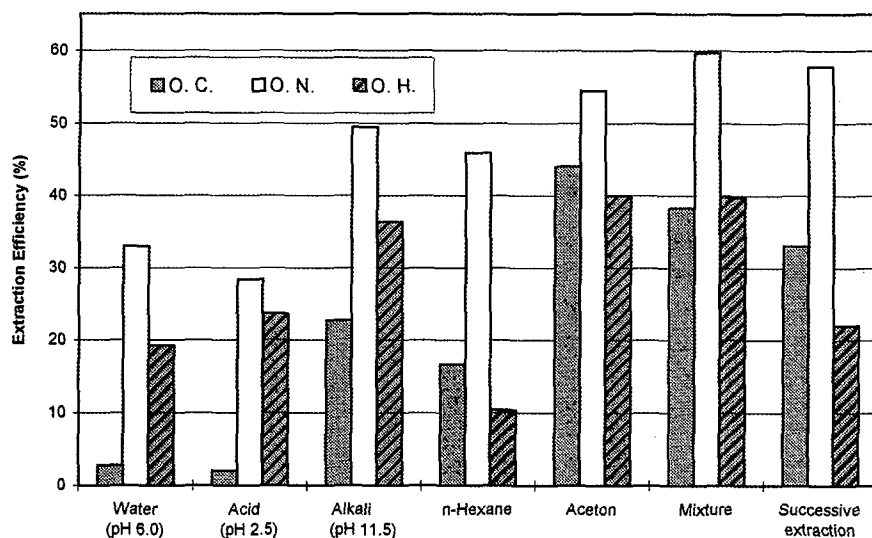


Fig. 2. The extraction efficiencies of organic compounds with various solvents in this study.

$$E.F.(non-polar) < E.F.(S.E.) \leq E.F.(Mixture) < E.F.(polar)$$

In this order, kinds of solvents are shown in parenthesis, and S.E. indicates the successive extraction, using acetone after n-hexane extraction in this study.

In these results, the comparison of E.F. of organic compounds between polar organic solvents and non-polar organic solvents indicates that organic compounds in urban aerosol sample of this study, include significant fraction of polar organic compounds. This is a critical point to estimate emission sources of organic compounds from urban aerosol samples and be discussed, in detail, in the following section.

E.F. with the acidity of water: In the atmosphere, the most dominant solvent is water, thus the solubility characteristics of organic compounds for water, are a critical point to decide the environmental contribution of organic compounds. In recent years, several empirical studies reported that some organic compounds in atmospheric particles, can be soluble in water (Saxena *et al.*, 1995; Novakov and Penner, 1993). Thus, some investigators measured the amount of particulate organic carbon extracted in water (Grojean, 1975) and

quantified the friction of the total particulate carbon in the sample that was extractable in water (Cadle and Groblicki, 1982). However, these studies were concentrated on the organic carbon, and the study for other organic compounds was sparse. In this study, in order to evaluate the solubility characteristics of organic compounds for the water, E.F. of organic carbon, -nitrogen, and -hydrogen were measured using an elemental analyzer. In addition, the pH of water which is the weak acidified water of pH 2.5, the water of pH 6.0, and the weak alkaline water of pH 11.5, was considered as the solubility factor for the E.F. of organic compounds, because the pH of water was thought to be important considering that the pH in water can affect the property of water solubility. Table 1 and Fig. 2 which were shown in previous pages, indicate E.F. of organic carbon, -nitrogen, and -hydrogen for the water. In these results, even though E.F. of organic compounds selected in this study, are different with the acidity of water, it is certain that some organic compounds in urban aerosol sample, can be soluble in water. In comparison with the acidity of water, E.F. of organic compounds selected in this study are higher in high pH of the alkaline water than in low pH of the

acidified water. However, E.F. of organic carbon, -nitrogen, and -hydrogen did not show significant difference in the comparison between the pH 6.0 of water and the pH 2.5 of water. These results indicated that aerosol; sample which was extracted in this study, may include a significant fraction of acids because of the higher extraction efficiencies of organic compounds in the alkaline water of pH 11.5 than in the acidified water of pH 2.5

3.2 Concentrations of oxalic acid and trace metals

In aqueous solution, the dissolved organic compounds can react with trace metals and then can form organic-metal complexes. In this study, oxalic acid, Cu^{2+} , Fe^{2+} , Zn^{2+} were analyzed in extracts which are from solvent extractions. In particular, concentrations of oxalic acid, Cu^{2+} and Zn^{2+} were used to estimate concentrations of oxalic-metal complexes in aerosols.

Oxalic acid was analyzed in water extracts and the concentration of oxalic acid was $3.9 \mu\text{g/g}$ in aerosol collected in this study. In addition, table 2 shows the amount of trace metals extracted by various solvent from 100 mg of aerosol sample. As expected, the extracted amount of trace metals are highest in acid water of pH 2.5 expect Zn^{2+} . In the case of Zn^{2+} , the extracted amount is slightly higher in the extraction using water of pH 6.0 and successive extraction than in the extraction using acid water of pH 2.5.

Table 2. The amount of trace metals extracted from 100 mg aerosol samples using various solvents.

Solvents	Zn^{2+} (mg)	Cu^{2+} (mg)	Fe^{2+} (mg)	Total (mg)
Acid water of pH 2.5	0.16	0.07	1.08	1.31
water of pH 6.0	0.20	0.05	0.54	0.79
Alkaline water of pH 11.5	0.04	0.01	ND	0.05
Acetone	0.14	0.05	0.42	0.61
n-Hexane	0.05	ND	ND	0.05
Binary mixture*	0.08	ND	0.24	0.32
Successive extraction**	0.20	0.07	0.30	0.57

Note: (*) The mixture of 50% volume of acetone and 50% volume of n-Hexane.

(**) The extraction using acetone after n-Hexane extraction.

In comparison for the concentration of trace metals in aerosols, Fe^{2+} is highest. In table 2, the amount of trace metals extracted from 100 mg of aerosol samples is lowest in n-hexane extraction, which is similar with extraction efficiencies of organic compounds explained in previous the section.

3.3 Estimation of emission sources for organic aerosol using extraction efficiency

The E.F. depend upon various types of solvent-solute interactions such as dipole orientation, dispersion forces, and hydrogen bonding. Also concerning with physical parameters characterizing the strength of the solvent, the E.F. can be related with dipole moment, dielectric constant, solubility parameter, and solvent strength. Therefore, E.F. are functions of the overall polarity of the solvent, which is the net effect of the various solvents-solute interactions. In the analysis of organic compounds from aerosol samples, the aerosol organic fraction contains numerous functional groups, thus no one organic solvent covers the complete polarity range of the aerosol organic compounds. However, using the principle that the best E.F. can be obtained when the polarities of the solvent and extractable compound are similar, it is possible to selectively extract organic compounds with the polarity of organic compounds. The polar solvent can selectively extract the polar organic compound and the nonpolar solvent can selectively extract the nonpolar organic compound.

If the selective extraction of organic compounds is considered, the result for E.F. of organic compounds with various solvents described earlier can be interpreted in terms of the fraction of polar and nonpolar organic compounds. Furthermore, the estimation of emission sources of organic compounds from the aerosol sample can be possible by the selective extraction using the polarity of solvent. Because, whilst non-polar compounds such as aliphatics, aromatics, polynuclear aromatics are associated with primary emissions, polar organic compounds such as carbonyl compounds, organic nitrates, mono- and dicarboxylic acids, and

difunctional compounds are associated with photochemical products. Therefore, it can be thought that non-polar solvent such as n-hexane can selectively extract non-polar compounds which are from primary emissions, also polar solvent such as acetone can selectively extract polar compounds which are photochemical products.

In this study, the extraction experiment for aerosol sample using the non-polar organic solvent such as n-hexane showed the lowest E.F. for organic compounds compared to the extraction of aerosol sample using other organic solvents such as polar organic solvent, the binary mixture of polar and non-polar organic solvents, and the successive extraction using polar organic solvent after non-polar organic solvent extraction. This result is similar with Grojean's and Daisey's studies, which showed that the E.F. of organic carbon was higher in polar organic solvents than in non-polar organic solvent. In particular, Grojean's study which evaluated E.F. of organic carbon with twenty-six of polar and non-polar solvents, included the evaluation of solvents E.F. as function of the ozone concentration averaged over the sampling period as shown in Fig. 3. In this figure, the solvent E.F. using polar solvents such as acetone and ethanol showed the increase as arise in the concentration of ozone, whilst the solvent E.F. using non-polar solvent such as iso-octane was constant as changing the concentration of ozone in ambient air. Considering that ozone is the representative of photochemical products in photochemical reaction, Grojean's study indicated that polar organic solvents can selectively extract polar compounds from urban aerosol sample. Therefore, the result of this study also indicates that compared to the primary organic compounds, organic compounds analyzed from urban aerosol sample in this study include a significant fraction of photochemical products which can be thought to be polar organic compounds. In this study, this suggestion can be supported by the other result which is about E.F. of organic compounds with the acidity of water.

In general, it was reported that the water-soluble

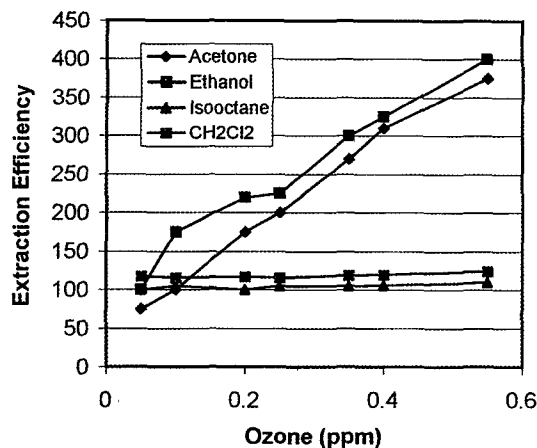


Fig. 3. Solvents extraction efficiencies (E.F.) as function of the ozone concentration averaged over the sampling period

fraction would consist of polar organics, whereas the benzene or cyclohexane-soluble fraction would contain non-polar organics (Saxena and Hildemann, 1996). In Fig. 2, E.F. of organic carbon, -nitrogen and -hydrogen are lower in water than polar organic solvent of acetone. However, E.F. of these organic compounds are higher in the alkaline water of pH 11.5 than in the non-polar organic solvent of n-hexane. Emission sources of polar organic compounds in the atmosphere are thought to photochemical reaction between hydrocarbons and ozone, whereas the non-polar organic compounds are from transportation, fuel oil combustion for power and space heating, and incineration. Considering the higher E.F. of organic compounds in alkaline water of pH 11.5 than in non-polar organic solvent of n-hexane, it can be thought that soluble compounds extracted by water may include different organic compounds from aerosol sample than nonpolar solvents and may be connected with the polar organic compounds. Therefore, these results support that organic compounds analyzed from urban aerosol sample in this study include significant fraction of photochemical products. In addition, another result of this study, which is the higher E.F. of organic compounds in alkaline water of pH 11.5 than

in water of pH 2.5 and pH 6.0, can support the presence of significant fraction of photochemical products within aerosol sample collected in this study. Because in the atmosphere, it can be thought that acids which can be soluble in alkaline water of pH 11.5, may be oxygenated compounds and these oxygenated compounds can be produced from the photochemical reaction in the atmosphere. In the atmosphere, acids can be divided into inorganic acids such as HNO_3 and H_2SO_4 , and organic acids such as photochemical products. However, considering that inorganic acids such as HNO_3 and H_2SO_4 can be soluble even in acid water of pH 2.5, it is thought that the alkaline water soluble fraction contains significant fraction of organic acids. Therefore it is certain that organic compounds in aerosol sample collected at UEA include a significant fraction of polar organic compounds which is thought to be photochemical products. This result indicates a key factor for selecting appropriate organic solvent for the extraction of aerosol samples.

In general, E.F. of organic compounds for the polarity of solvents are critical to analyze organic compounds from aerosol samples, because the extraction process is necessary to analyze organic compounds from the aerosol, and organic solvents, most often, are used to extract organic compounds from aerosol. Therefore it is important to decide suitable solvent for the objectives of the experiment. In terms of this view point, this study implies that if non-polar solvents are only used to extract organic compounds from urban aerosol sample collected in UEA, the aerosol organic fraction expressed in the part as non-polar solvent soluble, is seriously underestimated for oxygenated organics produced by photochemical reactions. This is of considerable importance for control strategies dealing with visibility degradation and adverse health effects associated with particulate organic matter.

3. 4 The complexion between oxalic acid and trace metals

In aqueous solution, the dissolved organic compounds can react with trace metals and then can form

organic-metal complexes. This complexion between organic compounds and trace metals can affect both the properties of organic compounds and the metals. In particular, aerosol contains about 30% of water in the percentage of weight, thus organic-metal complexes can be from within aerosol. In aerosol, the aqueous chemistry of oxalic-metal complexes was studied through the concentration of oxalic-metal complexes. These complexes which are CuHOx^+ , CuOx , $[\text{Cu}(\text{Ox})_2]^{2-}$, ZnHOx^+ , ZnOx , $\text{Zn}(\text{HOx})_2$, and $[\text{Zn}(\text{Ox})_2]^{2-}$, are considered in terms of oxalic acid, copper, and zinc. In these compounds, the oxalic acid is simply expressed as abbreviation. $[\text{H}_2\text{Ox}]$ is $[\text{COOH-COOH}]$, $[\text{HOx}^-]$ is $[\text{COOH-COOH}]^-$, and $[\text{Ox}^{2-}]$ is $[\text{COO-COO}]^{2-}$. Chemical reactions for the formation of these oxalic-metal complexes were shown in table 3 in Appendix.

In order to calculate the concentration of oxalic-metal complexes, Eq. 5, 6, and 7 shown in Appendix were used. In these equation, variables are $[\text{Cu}^{2+}]$, $[\text{Zn}^{2+}]$, and $[\text{HOx}^-]$, and all constants except these three variables can be decided. For example, all equilibrium constants can be get from literatures and $[\text{H}^+]$ can be decided by pH value in solution. Regarding total concentrations of oxalic acid, copper, and zinc in aerosol, concentrations of oxalic acid, copper, and zinc analyzed in this study were used to estimate. These concentrations of oxalic acid, copper, and zinc in aerosol are $3.9 \mu\text{m/g}$, $700 \mu\text{m/g}$, and $1600 \mu\text{m/g}$ in this study. As mentioned earlier, if it is assumed that aerosol contains about 30% of water concentrations ($\mu\text{m/g}$) of oxalic acid, copper, and zinc in aerosol can be converted into concentrations (mol/L) in water within aerosol. In the case of oxalic acid, the conversion of $\mu\text{m/g}$ to mol/L is shown as below:

$$\frac{3.9 \mu\text{m of oxalic acid}}{\text{g of aerosol}} \times \frac{1 \text{ g of aerosol}}{0.0003 \text{ L of water}} \times \frac{1 \text{ mol of oxalic acid}}{90000000 \mu\text{m of oxalic acid}} = 0.00014 \frac{\text{mol}}{\text{L}}$$

Therefore, $3.9 \mu\text{m/g}$ of oxalic acid can be expressed

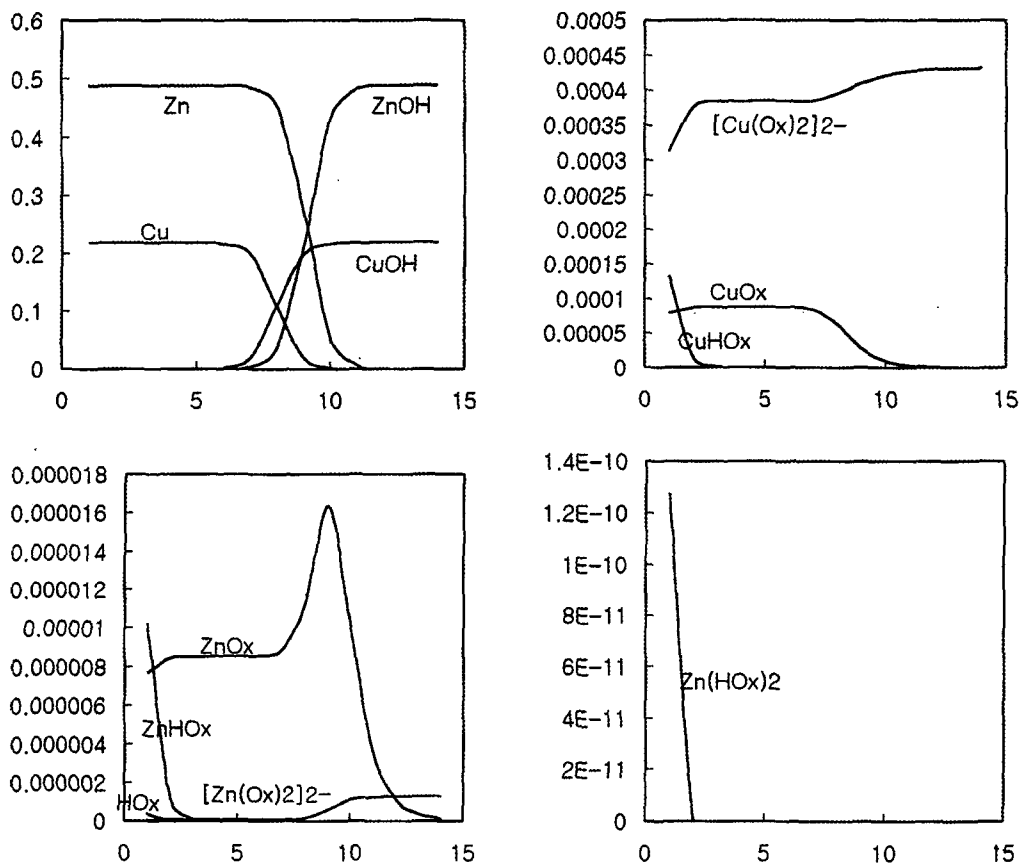
into 0.00014 mol/L using the assumption which is that aerosol contains about 30% of water. Also 700 $\mu\text{m/g}$ of copper and 1600 $\mu\text{m/g}$ of zinc can be converted into 0.037 mol L⁻¹ of copper and 0.082 mol/L of zinc.

In the study of complexation between oxalic acid and trace metals, total concentrations of reactions such as oxalic acid and trace metals are critical to decide products such as oxalic-metal complexes, HOx⁻ and Ox²⁻ which are forms of the hydrolysis of oxalic acid in solution. As mentioned earlier, the concentration of oxalic acid is much lower than the concentrations of copper and zinc. In order to estimate the aqueous chemistry of oxalic-metal complexation in aerosol, these concentration levels which are based on concentration

levels of oxalic acid, copper, and zinc analysed in this study, were used to calculate the production and the destruction of oxalic acid, copper, zinc, their complexes, HOx⁻, Ox²⁻. Therefore, oxalic-metal complexes in this study were estimated under the condition which is that the concentration of oxalic acid is much lower than concentrations of copper and zinc in aerosol.

3.5 The variation of oxalic-metal complexes and trace metals with pH

Using 0.00014 mol/L of oxalic acid, 0.037 mol/L of copper, and 0.082 mol L⁻¹ of zinc for TOx, TCu, and TZn, Eq.5, 6, and 7 shown in Appendix can be



Total concentrations: Oxalic acid(0.00014 mol L⁻¹), Copper(0.037 mol L⁻¹), Zinc(0.08 mol L⁻¹); 30% of water in aerosol

Fig. 4. The variation of the concentration of oxalic-metal complexes with pH in aerosol.

resolved for $[\text{Cu}^{2+}]$, $[\text{Zn}^{2+}]$, and $[\text{HOx}^-]$ with pH 1~14. Fig. 4 indicates concentrations of compounds considered in this study for oxalic-metal complexes with pH. Concentrations of copper and zinc are higher in acid of low pH than in alkaline of high pH. As expected, most metals are complexing with OH^- in solution as increasing pH, because the concentration of OH^- in alkaline solution is much higher than the concentration of oxalic acid, even through equilibrium constants between metals and H_2O are lower than equilibrium constants between metals and oxalic acid, which are shown in table 3 in Appendix. However, the most increasing fact in Fig. 4 is the concentration of $[\text{Cu}(\text{Ox})_2]^{2-}$. The total concentration of oxalic acid obtained during this study was $0.00014 \text{ mol L}^{-1}$ in aerosol, and Fig. 4 shows that the concentration of $[\text{Cu}(\text{Ox})_2]^{2-}$ is $0.0000697 \text{ mol L}^{-1}$ in alkaline solution from pH 10. Considering the total concentration of oxalic acid and the concentration of $[\text{Cu}(\text{Ox})_2]^{2-}$, it can be thought that most oxalic acids exist in the form of oxalic-metal complexes in aerosol, in particular, in the form of $[\text{Cu}(\text{Ox})_2]^{2-}$. In previous study, it was thought that oxalic acid exist under forms of hydrolysis such as HOx^- and Ox^{2-} in aerosol (Clegg, *et al.*, 1996). however, the contribution of complexion between oxalic acid and trace metals has not been considered in previous study. This study, which considered the complexion between oxalic acid and trace metals, shows the possibility of organic-metal complexes in aerosol.

Therefore, oxalic acid in aerosol can exist in the form of metal complex under the presence of metals in aerosol, in particular, the presence of copper in aerosol.

4. CONCLUSIONS

In this study, the solubility characteristics of organic compounds were evaluated in terms of extraction efficiency as a function of the polarity and the acidity of solvent. In addition, after being dissolved in aqueous solution within aerosol, the aqueous chemistry of organic compounds were studied in terms of the

organic-metal complexion. In the study of organic-metal complexes, concentration of oxalic-metal complexes were calculated with pH to estimate the mass balance of oxalic acid in aerosol, and the effect of oxalic-metal complexion on the concentration of oxalic acid of the gas phase was evaluated. Conclusions are as shown below:

- The solubility characteristics of organic compounds can be affected by the polarity of solvent and the acidity of solvents.
- Some organic compounds are water soluble, even though they are much smaller than acetone soluble fractions.
- It can be thought that significant fractions of organic compounds analysed in aerosol are polar organic compounds due to the higher extraction efficiencies of organic compounds in acetone (polar solvent) extraction than in n-hexane (nonpolar solvent) extraction. Therefore, if nonpolar solvent will be used to extract organic compounds from aerosol sample, it can seriously underestimate the concentration of organic compounds due to the significant fraction of polar organic compounds in aerosol.
- Most oxalic acids are exist in the form of oxalic-copper complexes in aerosols collected in UEA

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Appendix: Estimation of oxalic–metal complexes

The complexation between oxalic acid and trace metals can be estimated through the mass balance of oxalic acid and trace metals in chemical reaction for the formation of oxalic–metal complexes ion aerosols. Oxalic acid (COOH–COOH) will be dissociated into hydrogen oxalate (COOH–COO⁻) and oxalate (COO–COO²⁻) in aqueous solution from within aerosol. Therefore, oxalic acid can exist in one of three forms with aerosol. In all chemical reactions and equations considered in this study, the oxalic acid is simply expressed as abbreviation. [H₂Ox] is [COOH–COOH], [HOx] is [COOH–COO⁻], and [Ox²⁻] is [COO–COO]²⁻. Table 3 shows all chemical reactions which were considered for the estimation of oxalic–metal complexes. In table 3, all 11 chemical reactions

were considered and all equilibrium constants except K₁, K₂, K_{O1} and K_{O2} were used from Martell and Smith’s study. Also equilibrium constants, K₁ and K₂ for the hydrolysis of oxalic acid were used from Clegg, etal’s study, and K_{O1} and K_{O2} for the complexation between OH⁻ and Cu²⁺ and Zn²⁺ were used from Stumm and Morgan’s study.

Oxalic–metal complexes in aqueous solution within aerosol were calculated using the mass balance of total concentration of oxalic acid and trace metals in aqueous solution. Total concentration of oxalic acid in aqueous solution can be shown in Eq.1, considering the chemical reaction with Cu²⁺ and Zn²⁺, and the hydrolysis of oxalic acid in aqueous solution.

$$[TOx] = [H_2Ox] + [HOx^-] + [Ox^{2-}] + [CuHOx^+] + [CuOx] + 2[(Cu(Ox)_2)^{2-}] + [ZnOx] + 2[(Zn(Ox)_2)^{2-}] + [ZnHOx^+] + [Zn(HOx)_2]$$

.....Eq.1

Also total concentration of trace metals such as Cu²⁺ and Zn²⁺ can be shown as Eq.2 and Eq.3.

$$[TCu] = [Cu^{2+}] + [CuHOx^+] + [CuOx] + [(Cu(Ox)_2)] + [CuOH]$$

.....Eq.2

$$[TZn] = [Zn^{2+}] + [ZnHOx^+] + [Zn(HOx)_2] + [ZnOx] + [(Zn(Ox)_2)] + [ZnOH]$$

.....Eq.3

Table 3. The summary of chemical reactions considered in this study for the calculation of oxalic–metal complexes.

Reaction Name	No	Chemical Reactions	Equilibrium Constant
Hydrolysis of oxalic acid	1	H ₂ Ox = H ⁺ + HOx ⁻	K ₁ = 5.29 × 10 ⁻²
	2	HOx ⁻ = H ⁺ + Ox ²⁻	K ₂ = 5.33 × 10 ⁻⁵
Complexion between oxalic acid and Cu ²⁺	3	Cu ²⁺ + Ox ²⁻ = CuOx	K _{C1} = 10 ^{6.23}
	4	CuOx + Ox ²⁻ = [Cu(Ox) ₂] ²⁻	K _{C2} = 10 ^{10.27}
	5	Cu ²⁺ + HOx ⁻ = CuHOx ⁺	K _{C3} = 10 ^{3.18}
Complexion between oxalic acid and Zn ²⁺	6	Zn ²⁺ + Ox ²⁻ = ZnOx	K _{Z1} = 10 ^{4.87}
	7	ZnOx + Ox ²⁻ = [Zn(Ox) ₂] ²⁻	K _{Z2} = 10 ^{7.65}
	8	Zn ²⁺ + HOx ⁻ = ZnHOx ⁺	K _{Z3} = 10 ^{1.72}
	9	Zn ²⁺ + HOx ⁻ = Zn(HOx) ₂	K _{Z4} = 10 ^{3.12}
Complexion between OH ⁻ , and Cu ²⁺ and Zn ²⁺	10	Cu ²⁺ + H ₂ O = CuOH ⁺ + H ⁺	K _{O1} = 10 ⁻⁸
	11	Zn ²⁺ + H ₂ O = ZnOH ⁺ + H ⁺	K _{O2} = 10 ^{-9.1}

In Eq.1, Eq.2 and Eq.3, each term can be recognized by $[HOx^-]$, $[Cu^{2+}]$ and $[Zn^{2+}]$ assuming equilibrium states of chemical reactions shown in table 3. Therefore Eq.1, Eq.2 and Eq.3 can be expressed a shown below:

$$\begin{aligned}
 [TOx] = & \frac{[H^+][HOx^-]}{K_1} + [HOx^-] + \frac{K_2[HOx^-]}{[H^+]} + KC_3[Cu^{2+}][HOx^-] + \frac{K_{C1}K_2[HOx^-][Cu^{2+}]}{[H^+]} \\
 & + 2\left\{ \frac{K_{C1}K_{C2}[Cu^{2+}]\{K_2[HOx^-]\}^2}{[H^+]^2} \right\} + \frac{K_{Z1}K_2[HOx^-][Zn^{2+}]}{[H^+]} + 2\left\{ \frac{K_{Z1}K_{Z2}[Zn^{2+}]\{K_2[HOx^-]\}^2}{[H^+]^2} \right\} \\
 & + K_{Z3}[Zn^{2+}][HOx^-] + K_{Z3}K_{Z4}[Zn^{2+}][HOx^-]^2
 \end{aligned}$$

.....Eq.4

$$[TCu] = K_{C3}[Cu^{2+}][HOx^-] + \frac{K_{C1}K_2[HOx^-][Cu^{2+}]}{[H^+]} + \frac{K_{C1}K_{C2}[Cu^{2+}]\{K_2[HOx^-]\}^2}{[H^+]^2} + \frac{K_3[Cu^{2+}]}{[H^+]}$$

.....Eq.5

$$\begin{aligned}
 [TZn] = & \frac{K_{Z1}K_2[HOx^-][Zn^{2+}]}{[H^+]} + \frac{K_{Z1}K_{Z2}[Zn^{2+}]\{K_2[HOx^-]\}^2}{[H^+]^2} + K_{Z3}[Zn^{2+}][HOx^-] + K_{Z3}K_{Z4}[Zn^{2+}][HOx^-]^2 \\
 & + \frac{K_4[Zn^{2+}]}{[H^+]}
 \end{aligned}$$

.....Eq.6

In Eq.4, Eq.5 and Eq.6, variables are all three which are $[HOx^-]$, $[Cu^{2+}]$, and $[Zn^{2+}]$. Except these three variables, all equilibrium constants considered in this tstudy were whown in table 3. Therefore, three equations such Eq.4, Eq.5 and Eq.6 can be resolved to calculate $[HOx^-]$, $[Cu^{2+}]$ and $[Zn^{2+}]$. Using these values of $[HOx^-]$, $[Cu^{2+}]$ and $[Zn^{2+}]$, oxalic-metal complexes which are $[CuHOx^+]$, $[CuOx]$, $[Cu(Ox)_2]^{2-}$, $[ZnHOx^+]$, $[ZnOx]$, $[Zn(HOx)_2]$, and $[Zn(Ox)_2]^{2-}$, can be calculated with pH.