Size distributions of low molecular weight dicarboxylic acids in atmospheric aerosols collected over Okinawa, Japan

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Abstract

Marine aerosols were collected at Cape Hedo, Okinawa, Japan (128.25°E, 26.87°N) using Andersen middle volume impactor (MVI) sampler at a flow rate of 100 L/min and pre-combusted quartz filter (80 mm in diameter). The aerosols were studied for low molecular weight straight chain (C2-C12) and branched chain (C4-C6) dicarboxylic acids and related compounds using a capillary gas chromatography after dibutyl ester derivatization. MVI sampler segregated aerosol particles at 9 stages (0.1-0.43, 0.43-0.65, 0.65-1.1, 1.1-2.1, 2.1-3.3, 3.3-4.7, 4.7-7, 7-11.3, and 11.3-50 µm in diameter) was used. Homologous dicarboxylic acids (C2-C12) and aromatic (phthalic) diacids were detected in the aerosols together with unsaturated dicarboxylic acids, ω-oxoacids (C2-C9) and α-dicarbonyls (glyoxal and methylglyoxal). In all the size ranges, oxalic acid (C2) was found as the most abundant dicarboxylic acid, followed by malonic (C3) and succinic (C4) acids. Glyoxylic (ωC2) acid, 2-oxoethanoic acid, was the most abundant ketoacid followed by pyruvic acid (Pyr). We found that all the water-soluble organic compounds are concentrated with peaks at fine particle sizes between 0.65µm and 1.1µm. Oxalic acid (C2, 0.24 to 70.53 ng.m⁻³, average of 21.51 ng.m⁻³) comprised 17% to 80% (average 63%) of the total diacid concentrations. The maximal concentrations of small diacids at particle sizes of 0.65 µm to 1.1 µm suggest that they are produced by gas-to-particle conversion via photochemical oxidation of precursor organics and subsequent condensation on the pre-existing fine particles during long-range atmospheric transport.
Acknowledgements

My internship was carried out from the 1st of April to the 29th of August in The Institute of Low Temperature Science, under the supervision of Kimitaka Kawamura.

I would sincerely like to thank everyone in the lab for their kindness, help and sympathy.
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I. INTRODUCTION

1. Background

As we look forward into the 21st century, humankind must make effective use of the limited resources available, conserve the global environment and mitigate the burden on the Earth to enable a sustainable lifestyle.

Currently, over six billion people live on the Earth, and the population continues to increase every year. The planet is home to many regions with diverse climates, weather and geographical and geophysical conditions, with different living environments and availability of resources such as water and energy. Even if these conditions were uniform throughout the world, every species living conditions would still be affected by political, economic, cultural differences. Human beings living in a variety of conditions must address a number of major challenges to enable a sustainable lifestyle. We must solve the global environmental problems that we currently face. Among other issues, atmospheric temperatures are increasing due to the enormous amounts of carbon dioxide gas released into the air as a result of our ever-increasing dependence on coal, oil, natural gas and other fossil fuels during the course for profits.

It is useless to mention that carbon dioxide, as a major contributor to the greenhouse effect, is now in the heart of the debate, but it is not the only responsible species for the current and coming climate changes.

In fact, aerosols, which are derived from anthropogenic, biogenic and marine biogenic sources, have been studied and analysed for more than 50 years now, as they appeared to be playing an important role in environmental issues.
2. Aerosols’ role in climate changes

Although long considered to be of marginal importance to global climate changes, tropospheric aerosol contributes substantially to radiative forcing, and anthropogenic aerosol in particular has imposed a major perturbation to this forcing. Both the direct scattering of short-wavelength solar radiation and the modification of the shortwave solar reflective properties of clouds by aerosols particles increase planetary albedo, thereby exerting a cooling effect on the planet.

**Aerosols have three majors effects :**

*Direct radiative forcing*: it has been recognized for over 60 years that aerosol particles influence the earth’s radiative balance directly by backscattering and adsorption of shortwave solar radiation\(^1\). Aerosol particles also absorb longwave (infrared) radiation, but this effect is usually small because the opacity of aerosols decreases at longer wavelengths and because the aerosols are most concentrated in the lower troposphere, where the atmospheric temperature, which governs emission, is practically the same as the surface temperature\(^2,3\).

*Indirect radiative forcing*: Clouds droplets form in the lower atmosphere by condensation of water on existing aerosol particles. Consequently, the concentration, size, and water solubility of the aerosol particles on which cloud droplets form, called Cloud Condensation Nuclei (CCN), have an immediate influence on the concentration and size of cloud droplets. These influences in turn affect the shortwave radiative properties of clouds that form on the aerosol, even in the absence of any influence on the macroscopic and thermodynamic properties of the clouds. Specifically, increased concentrations of CCN, result in increased concentrations of cloud droplets, resulting in enhanced shortwave albedo of clouds\(^4-9\).

*Cloud lifetime influence*: a decrease in mean droplet size associated with an increase in cloud-droplet concentration is also expected to inhibit precipitation development and hence to increase cloud lifetimes\(^10-14\). Such an enhancement of cloud lifetime and the resultant increase in fractional cloud cover would increase both the short and longwave radiative forcing of clouds. However, because this effect would predominantly influence low clouds, for which the shortwave influence dominates, the net effect would be one of a further cooling. Inhibited precipitation
development might further alter the amount and vertical distribution of water and heat in the atmosphere and thereby modify the earth’s hydrological cycle. Although these effects cannot yet be quantified, they have the potential of inducing major changes in global weather pattern as well as in the concentration of the dominant greenhouse gas itself, water vapor.

3. Aim of the project

The main purpose of this project was to analyse the size-distribution of low molecular weight (LMW) dicarboxylic acids to get an overview about the atmospheric situation in Okinawa, in order to better understand the origin and transformation of organic materials and their transport processes in the atmosphere. The photochemical processes for the formation of organic aerosols were also studied.

I focused on LMW dicarboxylic acids because such aerosols make up a substantial fraction of atmospheric fine particle matter, accounting for 30-70% of aerosol carbon mass in the lower troposphere\textsuperscript{15}.

The target molecules were LMW normal saturated dicarboxylic acid, branched saturated diacid, unsaturated diacid, hydroxylated diacid, oxodicarboxylic acids, ω-oxocarboxylic acids, ketocarboylic acids and dicarbonyls.

The choice of a size-segregated impactor sampler, is very important because it allows us to get deeper into the photochemical aging processes of organic aerosols and then get a better understanding of the big picture. By looking at the size-distribution of organic aerosols and certain ratios, we can better understand the transformation as well as the transport processes of organic aerosols.
Those molecules can come from primary emissions (e.g. fossil fuel combustion, biomass burning and cooking\textsuperscript{16-20}) but can be secondary photochemically produced in the atmosphere\textsuperscript{21-22} as well, by further oxidation by oxidants such as O\textsubscript{3}, HO\textsuperscript{•}, NO\textsubscript{3}.
II. Experiments

1. Sampling site

The samples were collected at Cape Hedo, Okinawa, Japan (128.25°E, 26.87°N) in between March 18th and April 13th 2008.

![Sampling site](image)

Figure 2. Sampling site.

2. Sampling method

The samples were collected using an Andersen middle volume impactor (MVI) sampler at a flow rate of 100 L/min and pre-combusted quartz filter (80 mm in diameter). This Middle Volume Impactor sampler segregated aerosol particles at 9 stages (0.1-0.43, 0.43-0.65, 0.65-1.1, 1.1-2.1, 2.1-3.3, 3.3-4.7, 4.7-7, 7-11.3, and 11.3-50 μm in diameter), in order to study the size distribution of organic aerosols.

A certain amount of air (100L/min) is pumped into the MVI, and at each stage, the size of the holes decreases, so the biggest particles are located in the first stage, while the smallest ones are located in the last stage.
5 sets of samples (9 samples per set) were collected, as well as 2 sets of filter blanks. However, only 4 sets of samples (MVI-002, MVI-003, MVI-004, MVI-005) and one set of filter blanks (MVI-001) have been analysed yet. After the sample collection, each filter was put in a precleaned glass jar with a Teflon-lined screw cap and stored in a freezer room at -20°C until the analysis.

Table 1. Filter sample ID and sampling information.

<table>
<thead>
<tr>
<th>Filter ID</th>
<th>Filter category</th>
<th>Start date</th>
<th>Start Time</th>
<th>Stop date</th>
<th>Stop Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>Okinawa MVI-001</td>
<td>Stage 1-8, backup</td>
<td>blank</td>
<td>18/03/2008</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Okinawa MVI-002</td>
<td>Stage 1-8, backup</td>
<td>sample</td>
<td>18/03/2008</td>
<td>16:44</td>
<td>23/03/2008</td>
</tr>
<tr>
<td>Okinawa MVI-003</td>
<td>Stage 1-8, backup</td>
<td>sample</td>
<td>23/03/2008</td>
<td>15:01</td>
<td>28/03/2008</td>
</tr>
<tr>
<td>Okinawa MVI-004</td>
<td>Stage 1-8, backup</td>
<td>sample</td>
<td>28/03/2008</td>
<td>19:04</td>
<td>02/04/2008</td>
</tr>
<tr>
<td>Okinawa MVI-005</td>
<td>Stage 1-8, backup</td>
<td>sample</td>
<td>02/04/2008</td>
<td>17:44</td>
<td>07/04/2008</td>
</tr>
<tr>
<td>Okinawa MVI-006</td>
<td>Stage 1-8, backup</td>
<td>sample</td>
<td>10/04/2008</td>
<td>16:40</td>
<td>13/04/2008</td>
</tr>
<tr>
<td>Okinawa MVI-007</td>
<td>Stage 1-8, backup</td>
<td>blank</td>
<td>13/04/2008</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
3. Backward air masses trajectories

10-days backward trajectories of air masses were calculated for starting heights of 500, 1500, 2000m, using the NOAA HYSPLIT service (http://www.arl.noaa.gov/ready). Based on the backward trajectories, I distinguished two main sources of air: one from continental regions (mostly Siberia and North-East China) and the other one from Pacific Ocean and Sea of Japan, categorized as marine air masses. But, because 3 to 5 days samples were collected, every single sample contains both air masses from continental and oceanic regions.

![Figure 4](image_url)  
Figure 4. Examples of backward air-masses trajectories with marine and continental air.

4. Analytical procedure

An aliquot (one quarter) of the filter was cut into small pieces and extracted with Milli Q water (organic free) under ultrasonification to separate water soluble dicarboxylic acids and other polar organic compounds. The water extracts were...
passed through a Pasteur pipet packed with quartz wool to remove particles and filter debris and then concentrated nearly to dryness using a rotary evaporator under a vacuum. The extracted dicarboxylic acids were esterified with 14% BF$_3$/n-butanol at 100°C for 1h. During this procedure, the carboxyl functional group was derived to butyl ester, and the aldehyde group was derived to dibutoxy acetal$^{23}$. The reaction products were extracted with 5 mL of n-hexane after adding 3 mL of pure water and acetonitrile (0.3 mL). The hexane layer was further washed with pure water (3 mL x 2) and concentrated to 50 µL in n-hexane in a 1.5 mL glass vial with a Teflon-lined screw cap.

The derivatives were analyzed with a capillary gas chromatograph (Helwett-Packard HP 6890) equipped with a split/splitless injector, a HP-5 fused silica capillary column (0.2 mm i.d x 250 m x 0.52 µm), and an FID detector. The column oven temperature was programmed from 50°C (2 min) to 120°C at 30°C/min and then to 310°C (20min) at 6°C/min. Injection temperature was maintained at 250°C. The GC peak areas for the derivatives were calculated with a Shimazdu C-R7A data system.
III. Results & discussion

1. Molecular distribution

In the Okinawa samples, we detected aliphatic saturated and unsaturated diacids as well as aromatic acids. The average concentrations of the determined dicarboxylic acids are listed in table 2.

Total concentrations of diacids ranged from 1.90 to 101.95 ng.m\(^{-3}\) with an average of 6.72 ng.m\(^{-3}\). The most abundant diacid was oxalic acid (C\(_2\)) whose concentration ranges from 0.24 to 70.53 ng.m\(^{-3}\) with an average of 21.51 ng.m\(^{-3}\). Its relative abundance in the total diacid (C\(_2\)-C\(_{12}\)) fluctuated from 17% to 80% (average 63%) depending on the impactor stage. The second most abundant diacid, on an average basis was found as malonic acid (C\(_3\), 9-26%, average 16%), followed by succinic acid (C\(_4\), 6-32%, average 12%). Abundances of the individual species decreased with an increase in carbon chain length, although adipic acid (C\(_6\)) and azelaic acid (C\(_9\)) are relatively abundant, 0.7-10% (average 4%) and 0.3-7% (average 2%) of the total diacids, respectively. In addition to the normal saturated species and aliphatic unsaturated and aromatic diacids, ketocarboxylic acids (0.55-13.47 ng.m\(^{-3}\), average 1.84 ng.m\(^{-3}\)) and α-dicarbonyls (0.02-2.30 ng.m\(^{-3}\), average 0.53 ng.m\(^{-3}\)) were detected as well. Glyoxylic acid (C\(_2\)\(\omega\), 0.01-9.4 ng.m\(^{-3}\), average 2.38 ng.m\(^{-3}\)) is the dominant ketocarboxylic acids followed by pyruvic acid (Pyr, 0.04-1.69 ng.m\(^{-3}\), average 0.63 ng.m\(^{-3}\)). Such characteristics, as the dominance of oxalic acid have been reported in several circumstances in the available literatures\(^{16,21,24-35}\).

The concentrations of the detected compounds are about 10 times lower than those in urban areas like Tokyo, Vienna, Leipzig, Beijing, Hong-Kong\(^{24,29,36-38}\) and are comparable with the concentrations of remote marine aerosols, and artic aerosols\(^{21,31}\). But, the fact that malonic acid is the second most abundant compound is a characteristic feature of marine aerosols and is different from the continental aerosols, where succinic acid is generally the second most abundant diacid following oxalic acid\(^{22,27,29,39-41}\).
Figure 5. Molecular distributions (average) of diacids and related compounds during the campaign.

Figure 6. Molecular distributions (average) of diacids (except for C$_2$), ketoacids, and dicarbonyls in four sets of Andersen impactor samples.
Table 2. Concentrations of LMW dicarboxylic acids, ketocarboxylic acids, and \( \alpha \)-dicarbonyls in Okinawa aerosol samples sets.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Range</th>
<th>Average</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Dicarboxylic acids</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Oxalic, C2</td>
<td>0.24-70.53</td>
<td>21.51</td>
</tr>
<tr>
<td>Malonic, C3</td>
<td>0.31-10.60</td>
<td>4.01</td>
</tr>
<tr>
<td>Succinic, C4</td>
<td>0.45-7.47</td>
<td>2.7</td>
</tr>
<tr>
<td>Glutdic, C5</td>
<td>0.12-2.37</td>
<td>0.66</td>
</tr>
<tr>
<td>Adipic, C6</td>
<td>0.14-1.43</td>
<td>0.71</td>
</tr>
<tr>
<td>Pimelic, C7</td>
<td>0.01-0.28</td>
<td>0.1</td>
</tr>
<tr>
<td>Suberic, C8</td>
<td>0.00-0.06</td>
<td>0.01</td>
</tr>
<tr>
<td>Azelaic, C9</td>
<td>0.09-1.03</td>
<td>0.29</td>
</tr>
<tr>
<td>Sebacic, C10</td>
<td>0.00-0.11</td>
<td>0.03</td>
</tr>
<tr>
<td>Undecanedioic, C11</td>
<td>0.00-0.28</td>
<td>0.08</td>
</tr>
<tr>
<td>Dodecanedioic, C12</td>
<td>0.00-0.04</td>
<td>0.01</td>
</tr>
<tr>
<td>Methylmalonic, iC4</td>
<td>0.01-0.32</td>
<td>0.12</td>
</tr>
<tr>
<td>Methylsuccinic, iC5</td>
<td>0.02-0.41</td>
<td>0.17</td>
</tr>
<tr>
<td>2-Methylglutaric, iC6</td>
<td>0.00-0.35</td>
<td>0.07</td>
</tr>
<tr>
<td>Maleic, M</td>
<td>0.03-0.45</td>
<td>0.19</td>
</tr>
<tr>
<td>Fumaric, F</td>
<td>0.00-0.26</td>
<td>0.06</td>
</tr>
<tr>
<td>Methylmaleic, mM</td>
<td>0.00-0.52</td>
<td>0.13</td>
</tr>
<tr>
<td>Phthalic, Ph</td>
<td>0.04-3.76</td>
<td>1.11</td>
</tr>
<tr>
<td>Isophthalic, iPh</td>
<td>0.00-0.23</td>
<td>0.07</td>
</tr>
<tr>
<td>Terephthalic, tPh</td>
<td>0.03-1.47</td>
<td>0.38</td>
</tr>
<tr>
<td>Malic, hC4</td>
<td>0.00-0.09</td>
<td>0.03</td>
</tr>
<tr>
<td>Ketomalonic, C3,oxo</td>
<td>0.01-5.55</td>
<td>0.73</td>
</tr>
<tr>
<td>4-Ketopimelic, C7,4oxo</td>
<td>0.02-1.56</td>
<td>0.41</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td>1.90-101.95</td>
<td>6.72</td>
</tr>
<tr>
<td><strong>Ketocarboxylic acids</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Glyoxylic, C2( \omega )</td>
<td>0.01-9.40</td>
<td>2.38</td>
</tr>
<tr>
<td>3-oxopropanoic, C3( \omega )</td>
<td>0.00-0.20</td>
<td>0.02</td>
</tr>
<tr>
<td>4-oxobutanoic, C4( \omega )</td>
<td>0.03-1.64</td>
<td>0.37</td>
</tr>
<tr>
<td>9-oxononanoic, C9( \omega )</td>
<td>0.00-2.03</td>
<td>0.27</td>
</tr>
<tr>
<td>Pyruvic acid, Pyr</td>
<td>0.04-1.69</td>
<td>0.63</td>
</tr>
<tr>
<td><strong>Total Ketocarboxylic</strong></td>
<td>0.55-13.47</td>
<td>1.84</td>
</tr>
<tr>
<td><strong>( \alpha )-dicarbonyls</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Glycoxal, Gly</td>
<td>0.00-1.69</td>
<td>0.32</td>
</tr>
<tr>
<td>Methylglycoxal, MeGly</td>
<td>0.00-1.19</td>
<td>0.21</td>
</tr>
<tr>
<td><strong>Total ( \alpha )-dicarbonyls</strong></td>
<td>0.02-2.30</td>
<td>0.53</td>
</tr>
</tbody>
</table>


2. Size distribution

The size distributions of diacids, ketocarboxylic acids and α-dicarbonyls for each set of samples are presented in the following figures. Fine and coarse mode are defined as smaller and larger than 2.1 μm, respectively. The samples showed an unimodal size distribution. I found that all the water-soluble organic compounds were concentrated in fine particle sizes with a maximum in between 0.65 μm and 1.1 μm, which is defined as the droplet mode, because aerosols particles within this mode are mainly produced by droplet phase reactions, occurring in the smaller mode (<0.43 μm). The fact that the organic aerosols are predominately found in the droplet mode suggests that they are secondary species, photochemically produced through in-cloud processes during long-range transport.

Figure 8. Size distribution of dicarboxylic acids concentrations.
Figure 7. Size distribution of $\alpha$-dicarbonyls concentrations.

Figure 9. Size distribution of ketocarboxylic acids concentrations.
3. Photochemically aging processes

i. Malonic over succinic acid ratio

Malonic acid, as well as other diacids, is partly derived from the incomplete combustion of fossil fuels or from secondary atmospheric production. But, because malonic acid is thermally less stable than succinic acid due to its structure, the degradation of malonic acid in the combustion process is probably more significant than its production. This is the reason why malonic acid is less abundant than succinic acid in vehicular exhausts, and in other primary emissions. However, the molecular distribution of LMW diacids in the aerosols samples from Okinawa is different from those reported in the motor exhausts and urban areas, i.e, malonic acid is more abundant than succinic acid in Okinawa’s samples. This suggests that the atmospheric diacids analysed in this study are mostly derived from the secondary atmospheric production rather than from direct primary emissions from anthropogenic sources, including automobile exhausts.

In addition of that, further oxidation of succinic acid can lead to malonic acid, according to this scheme:

\[
\text{HOOC-CH(OH)-CH(OH)-COOH (succinic acid)} \xrightarrow{[\text{Ox}]} \text{HOOC-CH(OH)-COOH} \xrightarrow{[\text{Ox}]} \text{HOOC-COOH (malonic acid)} + \text{HOOC-COOH (oxalic acid)}
\]

Figure 10. Oxidation of succinic acid into malonic acid\textsuperscript{24}.

That is why, the C\textsubscript{3}/C\textsubscript{4} ratio is used in several studies as an indicator of enhanced photochemical production of dicarboxylic acids in the atmosphere\textsuperscript{21,24,29,38}. 

20
Table 3. Averaged C3/C4 ratios.

<table>
<thead>
<tr>
<th>Set</th>
<th>MVI-002</th>
<th>MVI-003</th>
<th>MVI-004</th>
<th>MVI-05</th>
<th>Average</th>
</tr>
</thead>
<tbody>
<tr>
<td>C3/C4</td>
<td>1.54</td>
<td>1.55</td>
<td>1.48</td>
<td>1.39</td>
<td>1.49</td>
</tr>
</tbody>
</table>

The ratios were almost constant during the period of sampling (20 days), except a small decrease with time. The higher concentrations of C₃ over C₄ indicate that malonic acid is mainly produced secondarily in the atmosphere by photo-induced reactions. However, the ratios were much smaller than 3, which is used as an index for secondary formation of dicarboxylic acids²¹,²⁹. But the average ratio is comparable with the C₃/C₄ ratio from Hong-Kong³⁸ which showed an average of 1.46. This can be an evidence of the fact that even if photochemically induced aging was the major process of organic aerosols production, there was still some primary organic aerosols brought to the sampling site in Okinawa.

**ii. Maleic over fumaric ratio**

Maleic acid is produced by photochemical oxidation of benzene whose cis configuration is preserved in the structure of the oxidation product. This has been supported by laboratories of photooxidation of aromatic hydrocarbons such as benzene and toluene⁴⁸,⁴⁹, in which maleic anhydride was detected. The maleic acid may further be isomerized photochemically to trans configuration (fumaric acid) in the atmosphere under solar radiation. By contrast, methylmaleic acid may be formed by oxidation of toluene, however, this species is unlikely to be isomerized to the corresponding trans configuration due to the presence of a methyl groupe, which interferes with the isomerization. This is consistent with the result that methylfumaric acid was not detected in aerosols samples, except for some samples collected in high Artic where, 2-methylfumaric acid was detected, at small concentrations⁵¹.
Figure 11. Oxidation of benzene and toluene into maleic acid and 2 methylmaleic acid, respectively, and further isomerization into fumaric acid concerning maleic acid.

The M/F ratio is controlled by the production of maleic acid and the subsequent transformation to fumaric acid. It is likely that, because photochemical production of maleic acid is enhanced in the summer, its production is much faster that the cis-to-trans isomerization, thus the M/F ratios are maintained to be higher. Okinawa is a sub-tropical island, the ambient temperatures were already close to summer temperatures (in between 20°C and 25°C) during the sampling campaign, from mid-March to mid-April 2008.

The M/F ratios were always higher than 2 during the campaign, from 2.69 to 4.00. We can reasonably assume that it is due to an increase in the solar radiation which is responsible for higher concentration of atmospheric oxidants and thus, higher production of maleic acid.

Table 4. Averaged M/F ratios.

<table>
<thead>
<tr>
<th>Set</th>
<th>MVI-002</th>
<th>MVI-003</th>
<th>MVI-004</th>
<th>MVI-005</th>
<th>Average</th>
</tr>
</thead>
<tbody>
<tr>
<td>M/F</td>
<td>2.69</td>
<td>3.19</td>
<td>3.26</td>
<td>4.00</td>
<td>3.28</td>
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</table>
4. Sources of aerosols

iii. C6/C9 and Ph/C9 ratios

As C₆ and phthalic acids are produced by the atmospheric oxidation of anthropogenic cyclic hexene and aromatic hydrocarbons such as naphtalene²⁴, whereas C₉ comes from biogenic unsaturated fatty acids²⁴, C₆/C₉ and Ph/C₉ ratios are used as indicators of source strength of anthropogenic and biogenic precursors to the aerosols diacids³⁸.

In Okinawa’s samples, C₆/C₉ (1.85-3.76, average 2.59) ratios were higher that those in Tokyo but lower that those in Los Angeles³⁸, which suggest that the analysed organic aerosols are mainly products of anthropogenic sources even if the relative contribution of anthropogenic to biogenic inputs in Okinawa is much less significant than in Los Angeles.

The same trend was observed for Ph/C₉ ratios (2.09-6.65, average 4.42), which implied an increase in the ratio and then, and important decrease. The peaks were around late March and early April, those could be relevant of a slight change in the sources of the detected aerosols. Showing an increase, and then a decrease, C₆/C₉ and Ph/C₉ ratios indicate an increased contribution of anthropogenic sources to the Okinawa aerosols in late March.

<table>
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<th>Set</th>
<th>MVI-002</th>
<th>MVI-003</th>
<th>MVI-004</th>
<th>MVI-005</th>
<th>Average</th>
<th>L.A</th>
<th>Tokyo</th>
<th>Hong-Kong</th>
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</thead>
<tbody>
<tr>
<td>C₆/C₉</td>
<td>1.85</td>
<td>3.76</td>
<td>2.71</td>
<td>2.05</td>
<td>2.59</td>
<td>7.4</td>
<td>0.72</td>
<td>0.91</td>
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<tr>
<td>Ph/C₉</td>
<td>2.09</td>
<td>4.93</td>
<td>6.65</td>
<td>4.00</td>
<td>4.42</td>
<td>8.0</td>
<td>0.83</td>
<td>6.12</td>
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</table>
Figure 12. Temporal variation of C6/C9 and Ph/C9 ratios.
IV. Conclusion and future works

Aerosol particles were collected with a Middle Volume Impactor, containing 9 stages, in Cape Hedo, on Okinawa, Japan, during early spring of 2008. A total of 45 samples with 3-5 days collections were obtained, and up to now, 36 were analysed. The sampled air could be divided in groups: air masses originating from North-East China and Siberia, air masses coming from Pacific Ocean or Sea of Japan. But the long-time samples did not allow us to separate the different air-masses.

Low molecular weight dicarboxylic acids, ketocarboxylic acids and α-dicarbonyls were studied. Oxalic acid was always the dominant species in all size segregated sample. All compounds classes showed an unimodal size distribution with maximum concentration on the droplet mode, between 0.65 and 1.1 μm aerodynamic diameters. This study demonstrates that small organic aerosols produced predominantly as submicrometer aerosols were produced by photochemically induced reactions, and in-cloud processes. Further studies are needed to better understand those processes, not well understood yet.

The ratio of C$_3$ to C$_4$, M to F, C$_6$ to C$_9$ and Ph to C$_9$ were used to distinguish primary and secondary sources, as well as source strength of anthropogenic and biogenic sources precursors in the atmosphere, respectively. C$_3$/C$_4$ and M/F ratios were strongly suggesting secondary sources for the detected aerosols. C$_6$/C$_9$ and Ph/C$_9$ were within the values reported for megacities (Los Angeles, Tokyo, Hong-Kong), suggesting an important contribution of anthropogenic inputs.

Further analysis, ion, organic carbon, total carbon, polycyclic aromatic hydrocarbons would be needed, in order to get more evidence of the photochemical reactions leading to such a size distribution.
V. References

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