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Appendix 3-1 Supplemental Materials for Seasonal Division

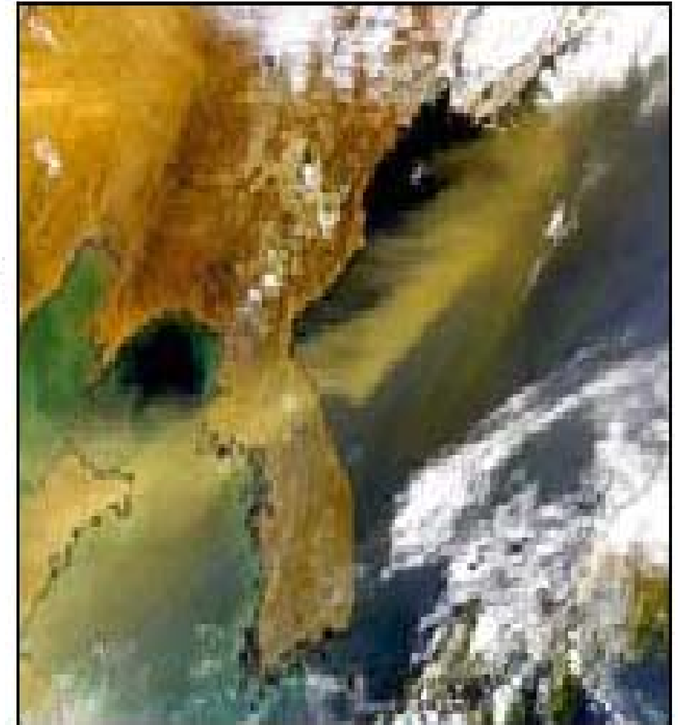
Asian Dust Storms Reach North America (April 18, 2001)

Huge dust storms that kicked up in Asia's Gobi Desert earlier this month have reached North America. The dust has spread across skies over 25% of the United States mainland. A dusty haze is visible from Alberta, Canada in the north to Arizona. Dust clouds have drifted eastward as far as the Great Lakes region.

After the dust clouds formed over the parched Gobi Desert sands, they picked up industrial pollutants over eastern China. The clouds then drifted across the Pacific Ocean.

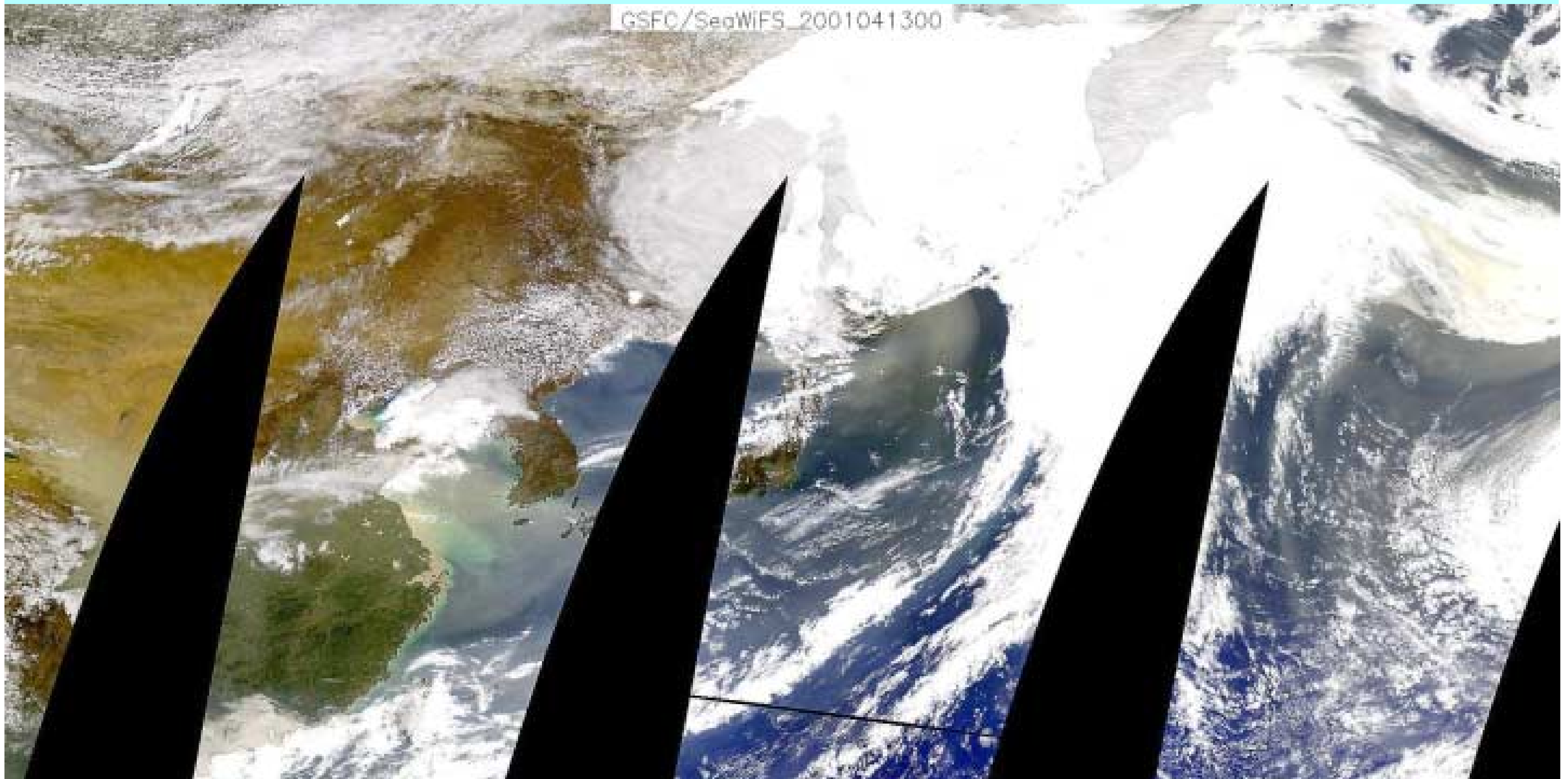
Progress of the dust clouds across North America is being monitored by SeaWiFS (Sea-viewing Wide Field-of-view Sensor) and other satellites.

Particles in the clouds reduce visibility and can trigger respiratory problems.

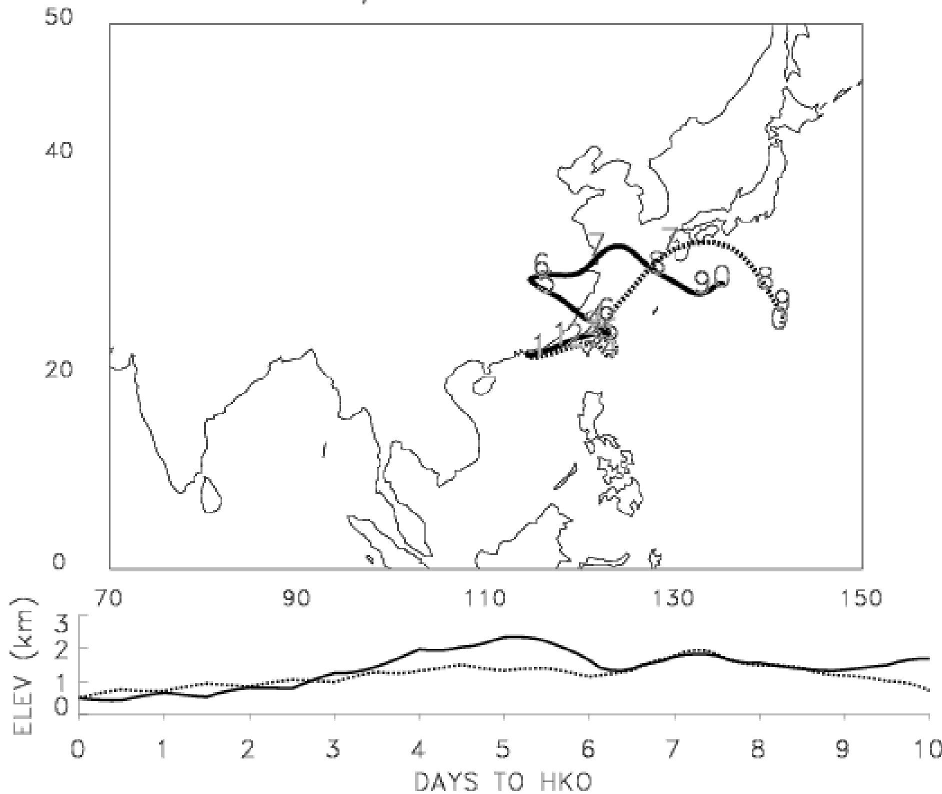


Brown-colored dust from recent Asian storms is visible moving across the Pacific Ocean. NASA/GSFC, SeaWiFS, and ORBIMAGE.

Satellite Image: April 10 – 16, 2001



The mid-April sandstorm came all the way to HK



FSP concentration at Tap Mun for April 2001

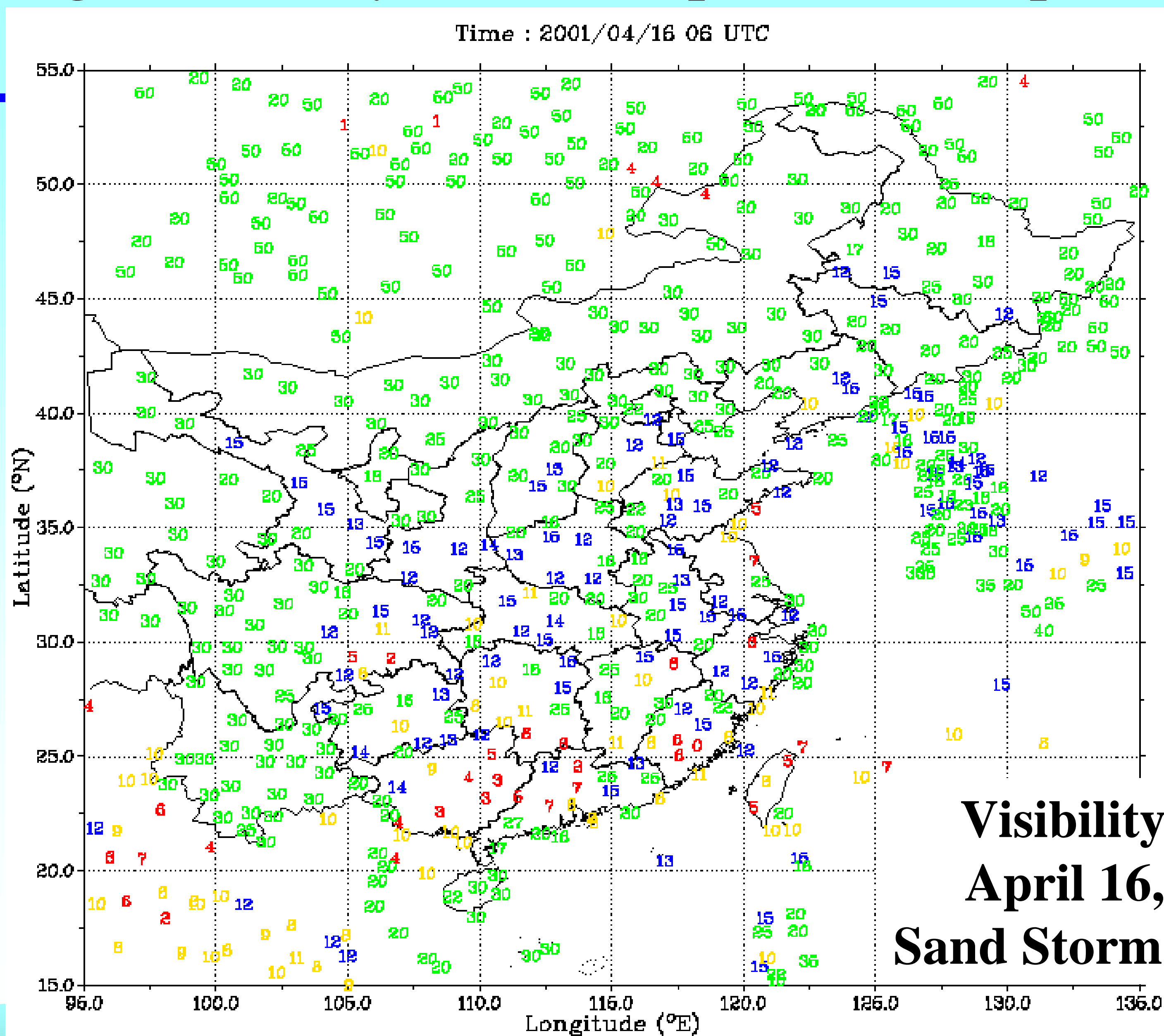
ug/m³

52.0
41.2
30.4
19.5
8.7
−2.1

0401
0408
0415
0422
0429

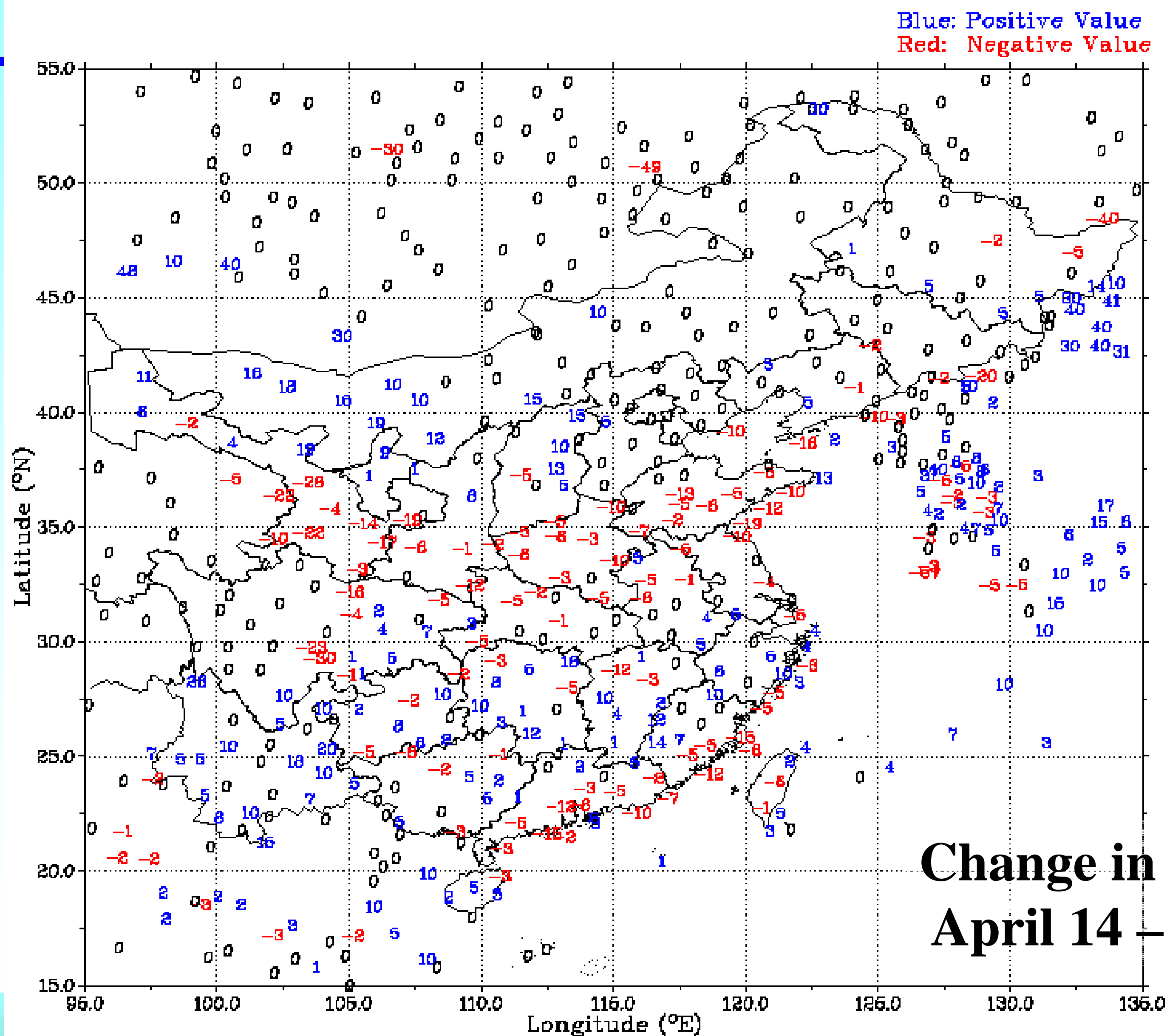
Time(MMDD)

Using Visibility to track pollution episodes



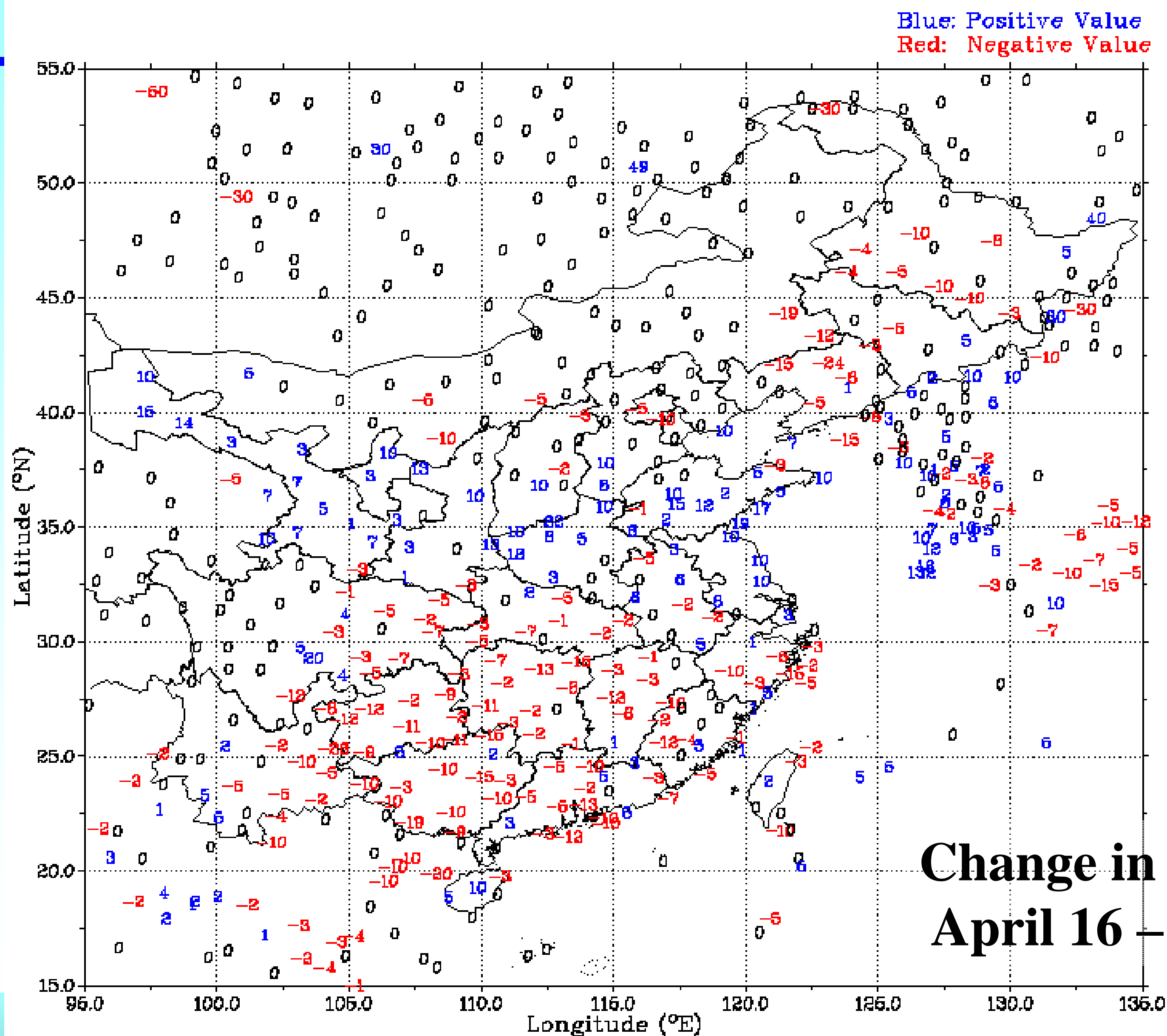
Visibility (km)
April 16, 2000
Sand Storm Episode

Using Visibility to track pollution episodes



Change in Visibility
April 14 – April 12

Using Visibility to track pollution episodes



Change in Visibility
April 16 – April 14

Appendix 4-1

Standard Operating Procedure for Dividing 47-mm Filters into Four Quarters using a Filter Cutter

Introduction

1. This document describes the proper use of a precision filter cutter (code: FC/E01) and the associated quality assurance procedures in handling of the cutter and filter samples.

2. The filter cutter is designed to cut a 47mm filter into four equal quarters. It has three components, a base, three razor blades, and a blade holder (see the drawing figure attached). The base consists of a base plate and a handle. The center of the base plate is a 47-mm circle, which is used for positioning the filter during cutting. The handle is used for applying pressure during cutting. The three razor blades consist of one long blade and two short ones, which are positioned perpendicularly to the longer blade. They are held in place in the blade holder by four screws. When the blade edge becomes dull, the blades can be replaced. Each time when a new set of blades are installed, it is necessary to ascertain the precision of the cutter according to the procedures as detailed in paragraphs 9 - 14 below.

Operating procedure

3. Follow the below procedures in cutting 47-mm filters using the precision cutter:

a) Prepare three 47-mm filter cassettes for each filter to be cut and label all the filter cassettes with the necessary information to identify the filter sample (i.e. sample code, date, etc). An example label can be 09Oct01_a, the last letter reserved to be a, b, c, or d to indicate the four quarters resulting from the filter division. (The filter cassette that holds the to-be-cut filter will be reused to hold one of the quarters after cutting).

b) The operator needs to wear disposable, PVC gloves and a mouth cover for the following steps.

c) Prepare a clean working surface using Al sheets pre-baked at 550°C overnight.

d) Prepare at least two pairs of forceps pre-baked or cleaned with methanol.

e) Clean the base plate, blade edges and the bottom surface of the blade holder according to the procedures as detailed in the quality assurance plan before use.

f) Place the to-be-cut filter and three pre-labeled empty cassette, with covers open, on the clean Al surface.

g) Use a pair of clean tweezers to remove a 47-mm filter from its storage cassette and place it in the 47-mm circle in the center of the base plate, with the particle-laden side up.

h) Fit the blade holder with the blades facing the filter into the two posts on the base plate.

i) Press down the handle on the top of the blaze holder for a few seconds.

j) Lift the handle and raise the blaze holder gently.

k) Gently flip the blaze holder to inspect if any filter pieces stick to the blade edges. (Note: A sudden flip action may cause a stuck filter piece to fall off from the blaze holder.) Remove any filter pieces on the blaze holder with a pair of forceps one by one and place each piece in one of the four cassettes on the bench, with the particle-laden side facing up.

l) Put the blaze holder with the blades facing up on a clean Aluminum sheet.

m) Examine the filter to make sure it has been divided into four pieces. In case of incomplete cut, use a clean razor blade to finish the cut.

n) Transfer the filter pieces on the base plate one by one to one of the four cassettes on the bench. The particle-laden side should always face upward.

o) Put the cover on for the four cassettes. The protruding ridge on the inside of the cover should press against the curved edge of the filter quarter and hold it rigidly in position. Stack the cassettes together and make sure that the particle side should always face upwards.

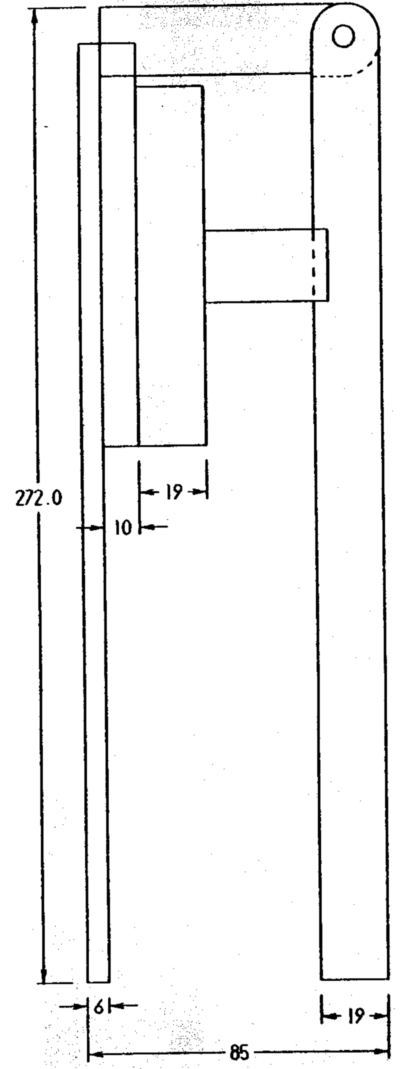
Quality Assurance Plan for application of the cutter

5. The cutter should be properly maintained and cleaned before use. Visual inspection should be conducted every time before using the cutter to ensure that the razor blades are sharp and the blade holder is in intact position. The cutter should be immediately withdrawn from use if defects are observed visually.
6. The precision of the cutter should be evaluated once every six months or after 1000 cuts. Records for the precision test should be properly documented.
7. Clean lens paper should be used for cleaning of the cutter blades. If necessary, the cutter could be cleaned with HPLC grade methanol, detergent water, rinsed with distilled water, and air-dried before use.
8. For every 20 samples or every batch, whichever is the less, a blank filter will be cut and analyzed as procedural blanks. The procedural blanks should not contain analytes of interest of concentrations greater than the respective detection limits.

Determination of the precision of the cutter

9. Prepare ten filters and ten 47mm filter cassettes. Label the filter cassette properly.

10. Cut ten filters following the same instruction as above.
11. Place all four quarters from the same filter in a 47-mm filter cassette.
12. Weigh each filter quarter at least twice using Sartorius MC5 microbalance or equivalent balance. Record the weight readings.
13. Use a standard excel worksheet to compute the relative standard deviation for the weight of the four quarters from a same filter. An example worksheet is attached.
14. The relative standard deviation for the weight of the four quarters should not be greater than 5 %. Otherwise, the cutter should be taken back to the workshop for re-adjustment.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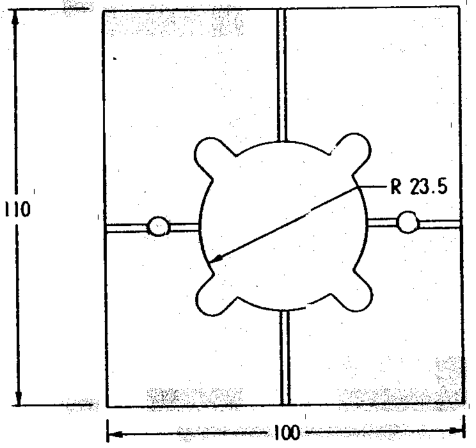
19
10
6
19
85


R 23.5
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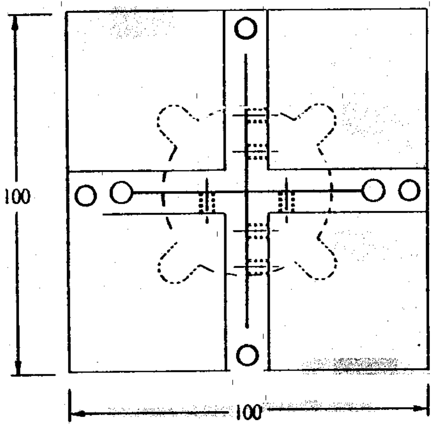
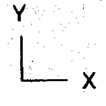
100


100
100


Y
X

Appendix 4-2

Extraction and analysis of water-soluble organic carbon in ambient aerosols

Treatment of apparatus (e.g. forceps, Al foil) before doing the experiment:

1. Bake the apparatus for 12 hours at 550°C.
2. Rinse with Milli-Q water, methanol and hexane in sequence. (This step is skipped for Al foil)

Treatment of glassware (e.g. beakers) before doing the experiment:

1. Wash the glassware with detergent.
2. Rinse with Milli-Q water.
3. Soak in hydrochloric acid for one day.
4. Rinse with Milli-Q water again.
5. Finally bake for 12 hours at 550°C.

Extraction of filter samples:

The seasonal composites consist of 26-80 quarter-filter pieces. The water extraction and volume reduction procedure is as follows:

1. Use a pair of tweezers to transfer 12-15 pieces of quarter-filters from their storage cassettes to an 25-ml Conical flask.
2. Add 10 ml of UV oxidized pure water (Barnstead Ultrapure Water System, Dubuque, IA, USA) to the flask using a 10-ml volumetric pipette. (Water used for extraction in the following steps has to be the purified water without any exception.)
3. Place the flask in an ultrasonic bath for 20 min. Ice water is placed in the ultrasonic bath to keep the water temperature below 10°C.
4. After sonication, pass the supernatant solution through a 0.2 mm pore size Teflon membrane syringe filter. (Keep the syringe filter for the next water extract of the same group of filters).
5. Discharge the filtrate into a 250 ml round bottom flask.
6. Repeat steps 2-5 for the same 12-15 pieces of filters. The filtrate is placed in the same 250-ml flask.
7. Discard the filter residue in the conical flask.
8. Steps 1-5 are repeated for the filters in the same seasonal composite. Water extracts are combined in the same 250-ml flask.
9. In the case that the final volume of the total water extract is less than 100 ml, add more water to make the final volume be 100 ml.
10. Connect the 100-ml water extract in the 250-ml flask with a rotary-evaporator. Evaporate water until the volume of the water extract is about 20 ml. It takes 1.6-2 hr for this step.
11. Transfer the ~20ml water extract to a 25-ml volumetric flask.
12. Rinse the 250-ml flask with two portions of 2 ml water and transfer the rinsing solution to the same 25-ml volumetric flask.
13. Fill the volumetric flask with water to the 25-ml mark.
14. Transfer the 25-ml water extract to a brown glass bottle with Teflon-lined cap.
15. Store the water extract in the freezer until analysis.

Sample pretreatment and analysis of WSOC:

1. Use one 5-ml and one 3-ml volumetric pipettes to withdraw 8ml water extract from its storage bottle and transfer to a 25-ml round bottom flask.
2. Connect the 25-ml flask with the rotary-evaporate. Evaporate the water extract to dryness. This step takes 20-30 min.
3. Add 500 µl water back to the 25-ml flask. Make sure to rotate the water so that the flask wall is thoroughly rinsed.
4. Use a syringe to withdraw 50 µl of the concentrated water extract and spike to a pre-baked 1.45 cm2 quartz filter punch.
5. Let the spiked filter air-dry. This takes ~30 min.
6. Place the dried filter punch on the quartz boat for the carbon analyzer and start the C analysis.
7. The conditions for the carbon analysis are as follows:
    - Purge the combustion chamber with 1% O2:99% He with the blower off for 20 sec.
    - Raise the front oven temperature to 600°C and keep at this temperature until 600 sec.
    - Raise the front oven temperature to 870°C and keep at this temperature until 120 sec has passed since the temperature ramp.

Appendix 4-3

Analysis of anions and cations in aerosol water extracts

The organic acids and inorganic anions are analyzed using a Dionex DX500 ion chromatograph with conductivity detector CD20 and gradient pump GP40. An IonPac AG11 guard column (4x50 mm) and an IonPac AS11 analytical column (4x250mm) are used to separate the analytes. An IonPac ATC-1 trap column (4mm, 9x24mm), and a Dionex ASRS-ultra 4mm anion self regenerating suppressor ensure the lowest possible background noise levels and detection limits. A sampling loop of 50ul is chosen for all the samples. The eluent is 0.2-5 mM NaOH (gradient) and the flow rate is 2 ml/min. The eluent gradient is as below:

Time 0 min. 6 min. 16 min. 30 min.
Conc. 0.2mM----0.2mM----5mM------5mM

The cations are analyzed using a Dionex DX500 ion chromatograph with electrochemical detector ED 40 and gradient pump GP40. An IonPac CG12 guard column 4x50mm and an IonPac CS12 analytical column 4x250mm are used. Dionex CSRS-ultra 4mm is used. The sampling loop is 50ul. The eluent is 20mM methanesulfonic acid. Isocratic elution at a flow of 1 ml/min is used and each analysis lasts 12 min.

Appendix 4-4

Analysis of amino acids and aliphatic amines in aerosol water extracts

Standard Operating Procedure:

Created on 10 Sep., 2001

Treatment of apparatus (e.g. forceps) before doing the experiment:

3. Bake the apparatus for 12 hours at 550°C.
4. Rinse with Milli-Q water, methanol and hexane in sequence.

Treatment of glassware (e.g. beakers) before doing the experiment:

6. Wash the glassware with detergent.
7. Rinse with Milli-Q water.
8. Soak in hydrochloric acid for one day.
9. Rinse with Milli-Q water again.
10. Finally bake for 12 hours at 550°C.

Reconstituting AccQ·Fluor Reagent:

1. A heating block is preheated to 55°C.
2. Tape Vial 2A lightly before opening to ensure all AccQ•Fluor Reagent Powder is at the bottom of the vial.
3. Rinse a clean micropipette by drawing and discarding 1ml of AccQ•Fluor Reagent Diluent from vial 2B.
4. Transfer 1.0ml of AccQ•Fluor Reagent Diluent 2B to the AccQ•Fluor Reagent Powder in vial 2A.
5. Cap the vial tightly.
6. Vortex for 10 seconds.
7. Heat Vial 2A on top of the heating block at 55°C until the AccQ•Fluor Reagent Powder is dissolved. (Do not heat the reagent for longer than 10 minutes.)
8. Store the reconstituted AccQ•Fluor Reagent in desiccators at room temperature up to one week.

Preparation for the internal standard solution (DL-Norleucine):

Note: The procedure is the same if a different –NH2 containing compounds is selected as the internal standard.

1. Weigh 32.795mg DL-Norleucine into a 25ml volumetric flask and dissolve it using 20mM HCl. This is 10 µM DL-norleucine stock.
2. Pipette 1ml 10 µM DL-Norleucine to a 10ml volumetric flask and fill with 20mM HCl to the mark. This is 1 µM (1000 pmol/µl) DL-norleucine stock solution.
3. Pipette 100 µl of the 1000 pmol/µl stock solution to a 5ml volumetric flask and fill with 20 mM HCl to the mark. This is 20 pmol/µl internal standard working solution.

Internal Standard (DL-norleucine)		
Required concentration	Calculation	Mass / Volume required
10 μM	0.01M*0.025L*131.18g/mol	32.795mg
1000 pmol/μl	0.001M*10ml/0.01M	1ml
20 pmol/μl	20pmol/μl*5ml/1000pmol/μl	100μl

Preparation of 2.5 mM Amino Acid standard mixture (AA Std mix-1 and AA std mix-2):

1. Dissolve the following individual AA or aliphatic amine standards in a 25 ml volumetric flask to make 10 mM stock solution.

53.91mg	D(+)-Galactosamine hydrochloride,
53.91mg	D(+)-Glucosamine hydrochloride,
22.27mg	Beta-Alanine,
24.39mg	Ethanolamine hydrochloride,
16.88mg	Methylamine hydrochloride,
25.78mg	D(-)-2-Aminobutyric acid,
20.39mg	Ethylamine hydrochloride
41.41mg	L(+)-Ornithine hydrochloride

2. Pipette 1.25ml of the above 10mM standard mixture to a 5ml volumetric flask and fill with water to the mark. This is the 2.5 mM Amino Acid standard mixture (AA std mix-1).
3. The commercially available AA standard mixture from Waters is AA std mix-2. Each AA standard in this mixture is supplied at a concentration of 2.5 mM except for cystein, which is supplied at 1.25 mM. The following 17 amino acids are included in this standard mixture:

L-alanine	L-leucine	Ammonia	L-lysine
L-methionine	L-arginine	L-phenylalanine	L-aspartic acid
L-proline	L-cystine	L-serine	L-glutamic acid
L-threonine	Glycine	L-tyrosine	L-histidine
L-valine	L-isoleucine		

Preparation of the 100 pmol/ul standard mixture:

1. Add 40μl AA std mix-1 into a clean autosampler vial. (The remaining 2.5mM AA standard mixture-1 can be stored at –20°C for up to 3 months.)
2. Add 40μl AA std mix-2 (2.5mM Waters Amino Acid Hydrolysate Standard into the same autosampler vial.
3. Add 920μl Milli-Q water to the vial. This is 100 pmol/μl stock calibration standard mixture. It can be stored at –20 ^{o}C for up to one month.

Preparation of 0.5, 2, 5, 20, 40 pmol/μl standards

1. 5, 20, 50, 200, and 400 μl of 100 pmol/ul stock calibration standard are added into five separate clean vials.
2. Add 995, 980, 950, 800, and 600 μl water, respectively, to make the final volume 1000ul.

Standard dilution			
Concentration of diluted standards (pmol/µl)	Calculation	Volume of 100 pmol/µl standard required (µl)	Volume of water required (µl)
0.5	1000µl*0.5pmol/µl / 100pmol/µl	5	995
2	1000µl*2pmol/µl / 100pmol/µl	20	980
5	1000µl*5pmol/µl / 100pmol/µl	50	950
20	1000µl*20pmol/µl / 100pmol/µl	200	800
40	1000µl*40pmol/µl / 100pmol/µl	400	600

Procedures for derivatization of the calibration standards:

1. Pipette 10µl of calibration standard and 10µl of internal standard (20 pmol/µl) in a 6 x 50 mm sample tube.
2. Add 160µl AccQ-Tag borate buffer.
3. Vortex for 10 seconds.
4. Add 20µl of AQC reagent solution.
5. Vortex immediately for 10 seconds.
6. Wait for 1 minute.
7. Transfer the content of the sample tube to a low volume insert (LVI) and cap tightly with a silicon-lined septum.
8. Remove the bubbles in the sample tube.
9. Heat the sample vial in a heating block for 10 minutes at 55°C.
10. Inject 20µl of the solution into the HPLC for analysis. Note: The derivatives can be stored at room temperature for up to one week.

Diluted standard concentration (pmol/µl)	0.5	2	5	20	40
Final standard concentration (pmol/µl)	0.025	0.1	0.25	1	2

Analysis of water soluble free amino acid in water extracts:

1. Prepare two sample tubes for each water extract sample.
2. Transfer 0.5ml water extract to each sample tube.
3. Evaporate the water extract to dryness under a gentle stream of argon gas or nitrogen gas (ultra high pure) at 40°C. This process takes about 2.5 – 3 hours.
4. Add 10µl internal standard solution (20pmol/µl) and 170µl borate derivatization buffer into the sample tube.
5. Vortex briefly the sample tube.
6. Gently purge the reconstituted sample solutions with ultra high purity argon gas or nitrogen gas for 50 minutes. The flow rate of gas must be controlled so that the volume loss of the sample solution won't exceed 30%. The purpose is to lower the

NH3 levels as a big NH3 peak would interfere the quantitation of the adjacent amino acid compounds.

7. Add 20 µl AccQ-fluorescence reagent solution into the sample tube and vortex immediately for 10 seconds.
8. After 1 minute of reaction, transfer the sample into a low volume insert (LVI) placed in an autosampler vial and cap tightly with a silicone-lined septum. The bubbles in the sample vial should be removed before heating.
9. Heat the sample vial to 55°C for 10 minutes prior to the HPLC analysis.

Analysis of hydrolysable combined amino acid:

1. Prepare two all-Teflon hydrolysis containers for each sample.
2. Add 1ml of water extract and 1ml constant boiling HCl (6N) to each Teflon hydrolysis vial.
3. Vortex for 10 – 20 seconds.
4. Seal the surface of the solution with Ultra high purity nitrogen gas for three times each for 2 minutes.
5. Screw the cap for the hydrolysis vial and place the vial in an oven at 110°C for 24 hrs.
6. Cool the sample to room temperature before open the cap.
7. Transfer 0.5ml post-hydrolysis sample solution to a sample tube.
8. Evaporated to dryness under a gentle stream of argon gas or nitrogen gas (ultra high pure) at 40°C.
9. Follow instruction for step 4 and onwards in the free AA analysis procedure.

Calculation:

Calibration curve:

$PR = m * C_{AA} + b$

Where PR is the peak area ratio, C_{AA} is amino acid concentration in unit of pmol/µl.

Amount of FAA & CAA in the water extract:

$C_{AA} = (PR – b) / m$

Amount of FAA (nmol) in x ml water extract = C_{AA}*200*(x/0.5)/1000

Amount of CAA (nmol) in x ml water extract = C_{AA}*200*(2/0.5)*(5/1)/1000

Amount of FAA and CAA expressed as air concentration

$$C(nmol/m^3) = C(nmol) * \frac{A_{filter}}{A_{water}} * \frac{1}{V(m^3)}$$

Where V is the sampled air volume, A_{filter} is the entire filter area, and A_{water} is the filter area used in water extraction.

Appendix 4-5.

Analysis of monomeric carbohydrates in aerosol water extracts

Standard Operating Procedure

1. Measurement Principle

Every molecule of sugar alcohol produces two molecules of formaldehyde upon periodate oxidation. The conversion of aldehyde and ketone sugars is accomplished through reduction by KBH4. Figure 1 illustrates the reaction scheme involved. The resulting formaldehyde is then derivatized by 2,4-dinitrophenylhydrazine (DNPH) and detected using reverse-phase DNPH-photo diode array detection.

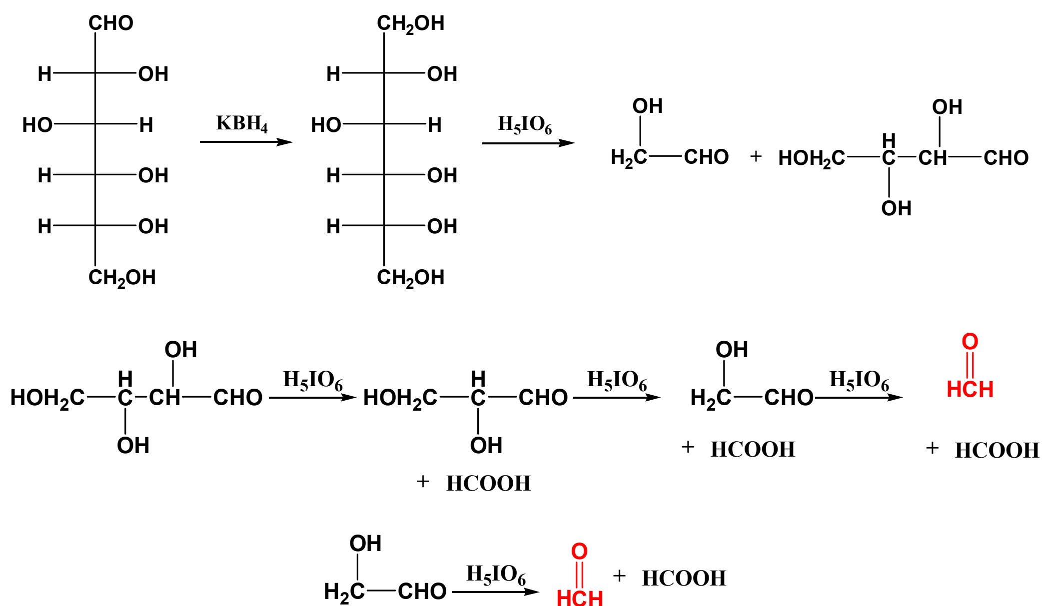


Figure 1. Reaction sequence of the formation of formaldehyde from a monomeric carbohydrate using glucose as an example

For the purpose of establishing calibration curves and checking the chemical degradation efficiency, formaldehyde and glucose are used as calibration standards each time when there is a need to analyze a batch of samples for total water-soluble monomeric carbohydrates. To correct for original formaldehyde on filter samples, each sample has to be analyzed for formaldehyde without going through the KBH4 reduction and periodate oxidation treatment.

1 Reagents & Standards

1. Formaldehyde, 37% aqueous solution, density 1.09 at 25°C.
2. Propanal (Internal standard)
3. 2,4-dinitrophenylhyazine

4. Acetonitrile, HPLC grade
5. Water, distilled and purified with the NANOPure Infinite UV model (Barnstead Ultrapure Water).
6. Glucose
7. Potassium borohydride (KBH4)
8. Sodium Periodate (NaIO4)
9. hydrochloric acid (HCl)
10. Sodium arsenite (NaAsO2)

2 Glassware and other labware

- 25-ml volumetric flask (1)
- 10-ml volumetric flask (1)
- 5-ml volumetric flask (many)
- 1ml pipette
- Erlenmeyer flasks

3 Apparatus

1. microbalance (weigh to 0.01 mg)
2. Oven (with temperature allowable > 150°C)
3. HPLC/photodiode array detector
4. 1.45 cm2 filter punch

4 Preparation of Reagent and standard solutions

4.1 10mg/ml KBH4 aqueous solution (MW 53.8) (0.186 M)

a. Weigh 50 mg of KBH4 to a 5ml volumetric flask,
b. add cold water to dissolve
c. fill to the mark.

(NOTE: This solution has to be made immediately before use.)

4.2 0.18N, 1N, and1.7N HCl

a. pipette 0.75ml 37% HCl solution (12.2N) into a 50 ml volumetric flask.
b. Fill with water to the 50-ml mark. This is the 0.18 N HCl solution.
c. Pipette 2.1 ml 37% HCl into a 25ml volumetric flask.
d. Fill with water to the 25-ml mark. This is the 1.0 N HCl solution.
e. Pipette 7.1 ml 37% HCl into a 50 ml volumetric flask.
f. Fill with water to the 50-ml mark. This is the 1.7 N HCl solution.

4.3 1 N NaOH

a. Weigh 1gram of NaOH into a 25 ml volumetric flask.
b. Dissolve with water and fill to the 25ml mark.

4.4 0.025M NaIO4 (MW 213.9)

a. Weigh 0.1337g of NaIO4 into a 25ml volumetric flask.
b. Fill with water to the 25ml mark.

4.5 0.25M NaAsO2 (MW 129.9)

a. Weigh 0.8119 g of NaAsO2 into a 25ml volumetric flask.
b. Fill with water to the 25 ml mark.

4.6 2000 ppm DNPH (MW 198) (10.1 mM).

a. Weigh 0.1 g DNPH into 1 50-ml volumetric flask.
b. Fill with acidic water to the 50-ml mark

4.7 313 ppm propanal

a. Withdraw 10 ul of propanal into a 25-ml volumetric flask.
b. Fill with water to the 25ml mark.

4.8 10.7 mM and 215uM formaldehyde stock solutions

a. **Withdraw 20 ul of 37% HCHO solution and add to a 25-ml volumetric flask.**
b. Fill with water to the 25-ml mark. This is the 10.8 mM formaldehyde stock solution.
c. Withdraw 200 uL of 10.7 mM HCHO solution and add to a 10ml volumetric flask.
d. Fill with water to the 10-ml mark. This is the 215 uM formaldehyde standard.

4.9 5mM and 100 uM glucose stock solutions

a. Use a microbalance to weigh ~22.5 mg of glucose to a 25ml volumetric flask.
b. Add water to dissolve the solid.
c. Fill with water to the 25-ml mark. This is the 5mM glucose standard.
d. Pipette 200ul of 5mM glucose standard to a 10ml volumetric flask.
e. Fill with water to the 10-ml mark. This is the 100 uM glucose standard.

5 Procedures

5.1 0-20 uM formaldehyde calibration standards

a. Prepare SIX 5-ml volumetric flasks.
b. Pipette 0, 25, 50, 100, 300, 500 ul of 215uM glucose stock solution to each 5-ml volumetric flask. This will be 0, 1.08, 2.16, 4.30, 12.90, and 21.50 uM formaldehyde calibration standard when the final volume is adjusted to 5ml.
c. Add 100ul 1.7 N HCl to each flask and 50 uL 2000 ppm DNPH and 10ul 313 ppm propanal.
d. Fill with water to the 5ml mark.
e. Wait for 1 hour and the standards are ready for HPLC analysis.

5.2 0-10 uM glucose calibration standards

a. Prepare SIX 5-ml volumetric flasks.
b. Pipette 0, 25, 50, 100, 300, 500 ul of 100uM glucose stock solution to each 5-ml volumetric flask. This will be 0, 0.50, 1.00, 2.00, 6.00, and 10.00 uM glucose calibration standard when the final volume is adjusted to 5ml.
c. Add 2, 2, 2, 1.9, 1.7, 1.5ml water to the above 5-ml volumetric flask to make the total volume about 2ml.
d. Add 50 ul 10mg/ml (0.186M) KBH4 to each flask.
e. Keep the flasks in the dark for 4 hours.
f. Add 50 ul 0.18N HCl to break down the excess KBH4.
g. Wait for 10 min to permit hydrogen gas to evolve.
h. Add 50 ul 0.025M NaIO4 and let the standards sit for 10 min at room temperature in a foil-covered rack.
i. Add 50uL 0.25M sodium arsenite to destroy the unreacted periodate and let the standards sit for 10 min at room temperature in the same foil-covered rack.

j. Add 100 ul 1.7 N HCl. A 20-min wait is given to allow the amber color evolved to disappear.
k. Add 50 uL 2000 ppm DNPH and 10ul 313 ppm propanal.
l. Fill with water to the 5ml mark.
m. Wait for 1 hour and the standards are ready for HPLC analysis.

5.3 Analysis of aerosol water extract for original formaldehyde

a. Pipette 2-ml of water extract to a 5ml volumetric flask.
b. Follow procedure 1c to 1e.

5.4 Analysis of aerosol water extract for total formaldehyde after KBH4 reduction and periodate oxidation

a. Pipette 2ml of the above water extract to a 5-ml volumetric flask.
b. Follow procedure 2d to 2m.

5.5 HPLC analysis

a. Transfer ~2ml of samples from procedures 1- 5 to autosampler vials and place in the autosampler tray in the HPLC system.
b. The HPLC conditions are set as follows:

Column:	Zorbax C_8 column
Mobile phase:	50% Acetonitrile & 50% water
Detector:	Photodiode array detector, 360 nm
Flow rate:	1.0ml/min
Injection Volume:	20 µL

6 Calculation

6.1 Calibration curves

1. Plot peak area ratios of formaldehyde to propanal versus formaldehyde and glucose concentrations in uM. (Note: The ratios are corrected for blank formaldehyde signal).
2. The resulting calibration curve slope for glucose should be ½ of the slope for formaldehyde. If it deviates for more than 10%, calibration should be re-done.

6.2 Original formaldehyde amount on filters

Measured HCHO concentration (uM)

$$C_{HCHO}(\mu M) = \frac{\frac{PA_{HCHO}}{PA_{IS}} - b_{HCHO}}{s_{HCHO}}$$

where PA_{HCHO} *and* PA_{IS} are the HPLC peak areas for formaldehyde and the internal standard.

b_{HCHO} and s_{HCHO} are the HCHO calibration interception and slope, respectively.

Amount of formaldehyde on each filter (umol)

$$m_{HCHO}(\mu mol) = [C_{HCHO}(\mu M) - B_{HCHO}(\mu M)] * 0.005(l) * \frac{x_ml}{2ml} * (\frac{A_{filter}}{1.45n})$$

Where B_{HCHO} is the HCHO concentration in the blank sample,

x is the total water extract volume,

A_{filter} is the surface area of a filter,
n is the number of 1.45cm^2 punches removed from a filter for water extraction.

6.3 Water-soluble monomeric carbohydrate concentrations

Measured glucose-equivalent concentration (uM)

$$C_{glu}(\mu M) = \frac{\frac{PA_{HCHO}}{PA_{IS}} - b_{HCHO}}{2 * s_{HCHO}} - \frac{C_{HCHO}(\mu M)}{2}$$

where PA_{HCHO} *and* PA_{IS} are the HPLC peak areas for formaldehyde and the internal standard with the KBH4-periodate procedure.

Amount of water-soluble monomeric carbohydrate on each filter (umol)

$$m_{MCH}(\mu mol) = [C_{glu}(\mu M) - B_{glu}(\mu M)] * 0.005(l) * \frac{x_ml}{2ml} * (\frac{A_{filter}}{1.45n})$$

Where B_{glu} is the HCHO concentration in the blank sample measured with the KBH4 reduction+ periodate oxidation procedure,
x is the water extract volume
A_{filter} is the surface area of a filter,
n is the number of 1.45cm^2 punches removed from a filter for water extraction.

Air concentration of water-soluble monomeric carbohydrates (nmol/m^3)

$$C_{MCH}(nmol/m^3) = \frac{m_{MCH}(\mu mol) * 1000}{V(m^3)}$$

Where $V(m^3)$ is the air volume collected.

Appendix 4-6

Analysis of aromatic acids, hydroxy acids, oxo-acids, and dicarbonyls

Preparation of PFBHA reagent

Prepare 19 mM PFBHA aqueous solution by weighing a known amount of PFBHA.HCl solid and dissolving in 5 ml water.

Preparation of calibration standards

1. Prepare a working stock solution in water at the level of 2 mM for each individual standard by weighing or pipetting a known amount of the chemical. The individual standards include lactic, glycolic, malonic, benzoic, maleic, succinic, glutaric, glyoxylic, malic, pyruvic, phthalic, azelaic, glyoxal, and methylglyoxal. All chemicals are used as it is purchased from manufacturors without further purification.
2. Prepare a stock solution of 2 mM D19-decanoic acid in 1:1 dichloromethane (DCM): hexane solvent mix. This chemical is used as internal standard (IS).
3. Pipette 100ul of each stock solution into a 10.00 ml volumetric flask to make a 20 uM of standard mixture
4. Take 100, 250, 500, and 1000ul of the 20uM standard mixture into four 2 ml vials. (The corresponding pre-injection final concentrations are 2, 5, 10, and 20 uM respectively for a final volume of 200 μl.)
5. Add 900, 750, and 500 ul of water into the first three standards, respectively.
6. Add 50 ul of the 19 mM PFBHA aqueous solution into each vial.
7. Leave the vials at the room temperature overnight.
8. Evaporate the standards to dryness using a gentle stream of UHP N2.
9. Add 200 ul of 10 uM IS into each vial.
10. Add 20 ul of BSTFA into each vial.
11. Place the vials in a heating block and heat them at 60°C for 40 min.
12. The samples are ready for injection after they are cooled to room temperature.

Preparation of samples

1. Pipette 0.5-1 ml of aerosol water extract to a 2-ml vial.
2. Follow procedure 6-12 in "Preparation of calibration standards.

GC/MS Analysis conditions (Varian 3400 GC/Star 2000 MS)

1. Injector temperature: 250°C

   split ratio and timing

Time (min.)	state	ratio
initial	off	off
0	off	off
2	on	100
2.5	on	30

2. Injection mode: std split/splitless

Pre-inj solvent flushes	0
Pre-inj sample flushes	1
Post-inj DCM/hexane flushes	10
Post-inj MeOH flushes	10

3. GC
   column flow rate: 1.00ml/min
   Temp. 60°C----------------210°C----------- ------280°C
   1 min. 8°C/min 0 min. 20°C/min 3min (total 26.25min)

4. MS parameter

Segment 1	Solvent delay	0-6 min.	
Segment 2		6-26.25min	m/z 40-650

Segment set points

Scan time (3 uscans)	1 seconds/scan
Emission current	10 uamps
Multiplier offset	0 volts
Count threshold	1 counts
Mass defect	0 mmu/100u

Ionization mode-EI auto

	Low mass	High mass	Ionization storage level (m/z)	Ionization time factor
1	10	99	35	100
2	100	249	35	100
3	250	399	35	100
4	400	650	35	100

Target TIC	20000 counts
Max. ionization time	25000 usec
Prescan ioniz. time	100 usec
Background mass	45 m/z
RF dump value	650 m/z