Annexure-A: Air Quality Sampling and Operational Procedure.

Air quality monitoring has been done with the speciation sampler to collect PM_{10} and $PM_{2.5}$ samples. Equipment operational details, working procedure, equipment and sample preparation and maintenance are discussed in detail below.

A-1 Speciation Sampler: Sampling of Particulate Matter PM_{10} and $PM_{2.5}$ from Ambient Air by Speciation Sampler

1.0 Scope

This procedure is applicable to air sampling for PM_{10} and $PM_{2.5}$ using speciation sampler on Teflon / Quartz filter paper.

2.0 Referred Documents

2.1 SOP MLD 055 by California Air Research Board

2.2 Model standard operating procedures (sops) for sampling and analysis by Central Pollution Control Board, New Delhi

2.3 Partisol® Model 2300 Speciation sampler manual by Rupprecht and Patashnick Co. Inc.

3.0 Significance and Use

This test procedure is used for collecting Particulate Matter 10 (PM_{10}) and Particulate Matter 2.5 ($PM_{2.5}$) from Ambient Air using Speciation Sampler Partisol 2300.

4.0 Apparatus

Following apparatus/ instruments were used:-

4.1 Partisol ® Model 2300 Speciation sampler manual by Rupprecht and Patashnick Co. Inc

4.2 Chemcomb Cartridge having Speciation impactor heads for PM_{10} and $PM_{2.5}$fractions

4.3 Filter papers (Teflon/ Quartz)

4.4 Proper (blunt) forceps

4.5 Labeled Filter paper petri dish for storing Filter paper

4.6 Sample Storage Kit

5.0 Chemicals/ consumables:

5.1 High Vacuum Grease

5.2 Teflon Filter: PTFE with Polymethyl pentane support ring, Micron size 1 um, 47 mm dia,

5.3 Quartz Filter paper: Binder free pure Quartz with high flow rate and filtration efficiency, 47 mm dia, Temp stability up to 1100^{0}C

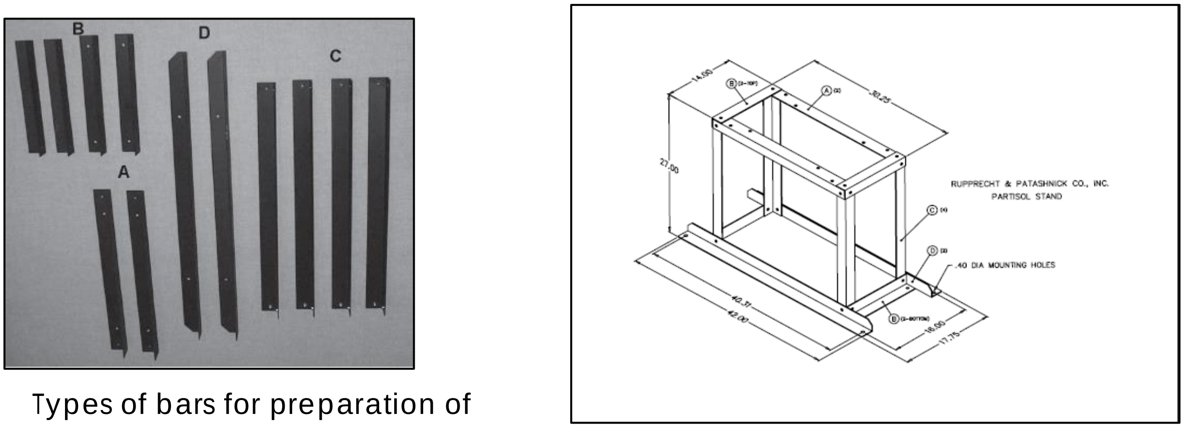
6.0 PPEs TO BE USED:

Cotton hand gloves, safety shoes

7.0 Procedure:

7.1 Install Partisol® Model 2300 Speciation sampler as per Manual on stand provided by Manufacturer (Refer Fig. A-1 for Sampler and Stand.)

Partisol® Model 2300 Speciation sampler mounted on stand



Types of bars for preparation of Stand

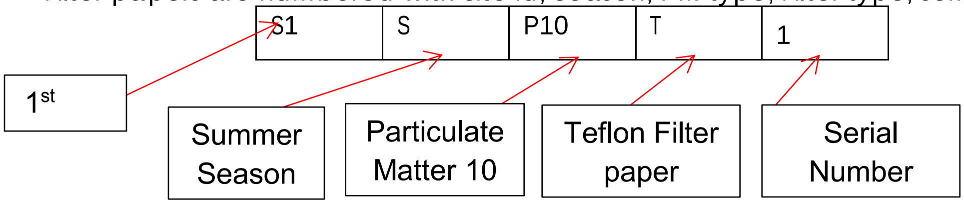
Partisol®2300 stand

Fig. A-1: Speciation sampler

7.2 Check Temperature and Humidity sensor connections.

7.3 Remove Chemcomb cartridge housing as per Fig. A-2

7.4 Filter papers are numbered with Site id, Season, PM type, Filter type, serial number.



Similarly for Winter Season ➔"W," PM2.5 ➔"P2.5" and Quartz filter paper ➔"Q"

7.5 Select filter paper as per above nomenclature. Visually inspect filter paper for any damages, pinholes or any other collection. If any anomalies are found then discard filter paper.

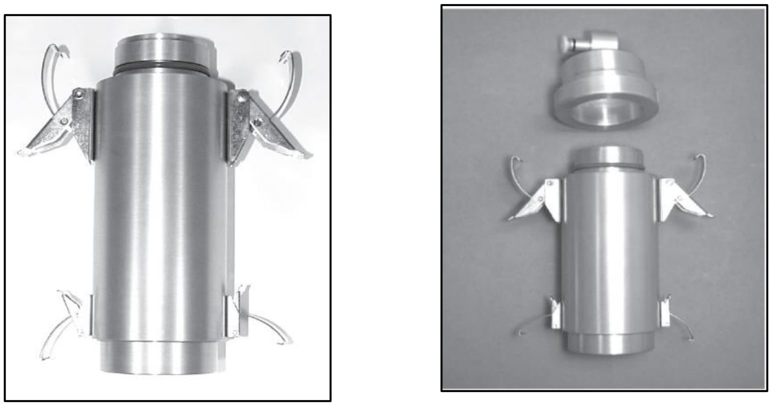
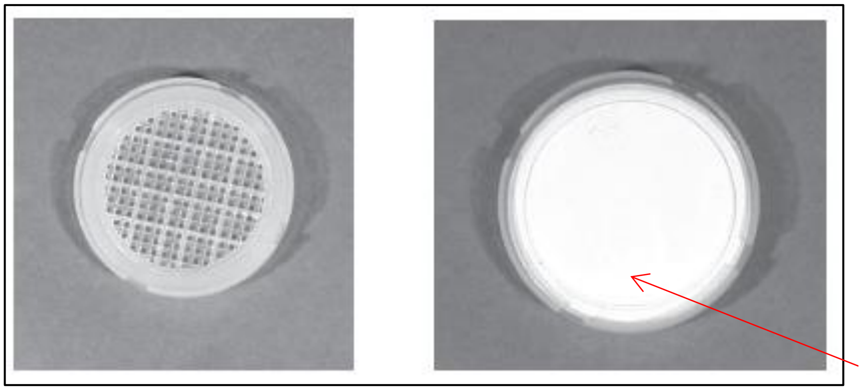


Fig. 2A: Chemcomb System Housing



Filter paper loaded in Plastic Ring

Fig. 2B: Filter paper kept inside plastic ring

Fig. 2C: PM2.5 head

Fig. 2D: Chemcomb cartridge mounting in sampler

Fig. A-2*:* Chemcomb cartridge system

7.6 Load filter paper in Chemcomb cartridge as per below table

Channel	PM head	Paper
A	10	Teflon
B	10	Quartz
C	2.5	Teflon
D	2.5	Quartz

7.7 Start Speciation sampler as per procedure given in A-2

A-2 Operational procedure for Speciation Samplers Partisol 2300

1.0 Sampler Start-up:

1.1 Install the ChemComb cartridges in the shelter.

1.2 Press the power switch (Fig A-1) on the main panel to activate the sampler.

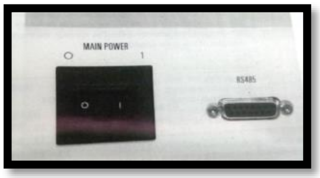


Fig. A-1: Power switch

1.3 If necessary, turn the adjustment knob, to adjust the brightness of liquid crystal display (LCD) (Fig.A-2).

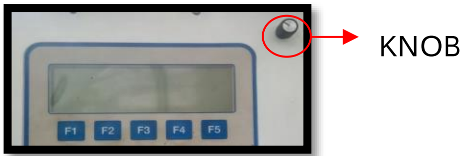


Fig. A-2: LCD Screen

2.0 Steps to program the sampler for a sampling run:

2.1 Install the desired number of ChemComb cartridges in the ChemComb shelter.

2.2 Ensure that main screen of sampler is in the Stop Mode and status OK.

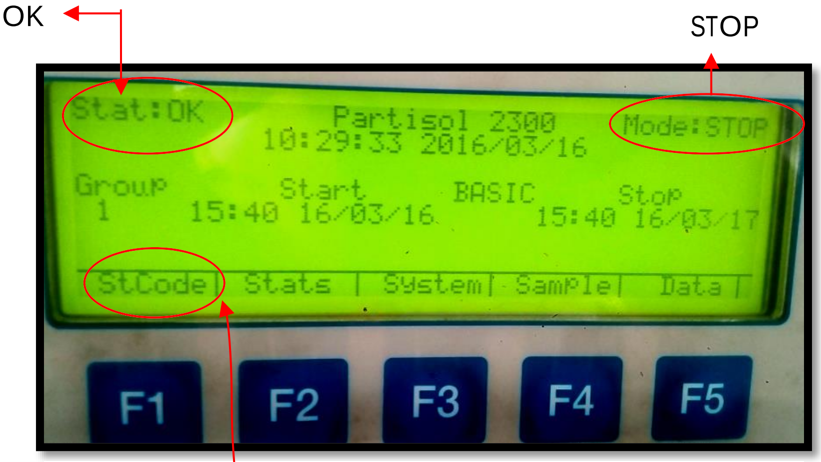


Fig. A-3: Main Screen

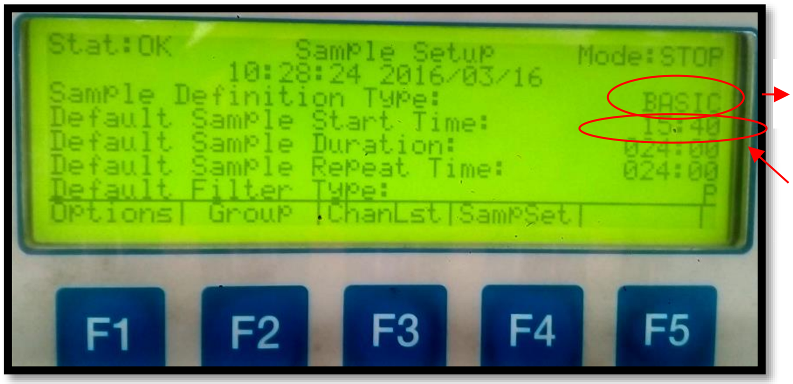
In the Main screen, press <F1: St Code> to display the Status Codes screen

Following are three types of status codes:

OK - No current status conditions.
Z - ***Power Failure***: A power outage occurred during sampling on the current filter.
U- ***User Pressed Stop***: The user pressed the <RUN/STOP> button during sampling.

2.3 While in the Status Code screen, ensure that the present status of the unit is "OK." Then press <ESC> to return to the Main screen. If status code is Z or U then press <F1> to reset it to OK and press ESC to return to main screen

2.4 While in the Main screen (Fig. A-3), press <F4: Sample> to enter the Sample Setup screen (Fig. A-4). Check whether sample definition is BASIC, if not then by pressing EDIT key change to BASIC. Then enter the start time for your sampling run(s), make sure that the start time is greater than the current time. Press <ENTER> to save these changes then press any key



```
Stat:OK        Sample Setup        Mode:STOP
          10:28:24 2016/03/16
Sample Definition Type:                BASIC
Default Sample Start Time:             15:40
Default Sample Duration:              024:00
Default Sample Repeat Time:           024:00
Default Filter Type:                       P
Options| Group |ChanLst|SampSet|
```

BASIC

START TIME

Fig. A-4: Sample setup screen

NOTE: When in the Edit Mode, use the arrow keys (<↑>, <↓>, <←> and <→>) to select the field that you want to edit. After you have finished editing the fields, press <ENTER> to save your changes

2.5 Check values of date and time for START and STOP for sampling run(s) in main screen (Fig 3). If the values are incorrect then press <F4: Sample> to enter the Sample Setup screen (Fig A-4) then go to start time by using arrow keys (<↑>, <↓>, <←> and <→>) further press EDIT key to change the start time and duration as per need, press <ENTER> to save changes. Press ESC to return to Main Screen.

2.6 Press <RUN/STOP> to start the sampling. If the start time is greater than current time system will show WAIT mode and sampling will start at correct programmed time.

2.7 Once the sampling starts, the system will show SAMP mode (Fig A-5) and Run time window will look like (Fig A-5).

```
Stat:OK      Partisol 2300      Mode:SAMP
         18:40:36 14/03/2016
Group: 1     BASIC Stop: 18:40 15/03/16
Chan 1A  Flow: 16.7 l/m  Vol:  0.008 m^3
Chan 1B  Flow: 16.7 l/m  Vol:  0.008 m^3
Chan 1C  Flow: 16.7 l/m  Vol:  0.008 m^3
Chan 1D  Flow: 16.6 l/m  Vol:  0.008 m^3
StCode| Stats | System| Sample| Data |
```

SAMP

Fig. A-5: Sampling screen

2.8 After sampling is finished, press Run/Stop key to stop sampling.

A-3 Data Retrieval of Data from Partisol 2300

1.0 steps to be followed to verify the sampling run status and retrieve the sampling run data:

1.1 If the sampler has not been previously set up for data transfer to a PC, check the RS232 setup in the RS232 Setup screen. Press <F3: System> from the Main screen to display the System Setup screen. Press <F1: I/O>, then <F1: RS232> to enter the RS232 Setup screen. Make sure that the parameter in the Protocol field is set correctly for the file transfer software installed in the PC (refer to Section 10.2.1 for setting RS232 parameters). Press <ESC> twice to return to the Main screen.

1.2 Connect the PC to the sampler with the 9-to-9 pin RS232 cable. Use any data transfer program such as Pro Comm Plus to transfer data from the sampler to the PC.

1.3 Check the sampling run status on the Main screen, and note any status code other than "OK." Press <F5: Data> to enter the Filter Data Statistics screen and view the filter data from the sampling run. Record data from the Filter Data Statistics screen onto a sampling run log sheet if desired. If there were any status codes other than "OK," check the Cartridge Data Status Codes screen to verify the validity of the sampling run.

1.4 While in the Filter Data Statistics screen, press <F1: MoreDat> twice to reach the Cartridge Data Status Codes screen. After checking the validity of the sampling run from this screen, press <ESC> until you return to the Main screen.

1.5 Press <F3: System> from the Main screen to display the System Setup screen. Press <F1: I/O>, then <F1: RS232> to enter the RS232 Setup screen. Press <EDIT> and set the Protocol field to **"Storage."** To save this change, press <ENTER>. Press <ESC> until you return to the Main screen.

1.6 Press <F5: Data> to display the Filter Data Statistics screen. The record from the last sampling run is displayed in the upper right hand corner of the Filter Data Statistics screen. Press <F5: DwnLoad> to display the Download Data screen. Scroll to the Last Record field, and use the <F4: Last> key to select the last data record. Scroll to the First Record field, and use the <F1: First> to select the first data record. Press the <F2: - Ptr> or <F3: +Ptr> key to select the first data record you want to download.

1.7 Once the PC communications software is ready to receive the records, press <F5: DwnLoad> while in the Download Data screen. The sampler will download all data from the currently displayed record to the last record in the data file. If you need to download output for interval data, status codes or any of the other screens accessed from the Filter Data screen, display the screen and repeat the download process.

1.8 If any status code conditions occurred, press <ESC> to return to the Main screen. From the Main screen, press <F1: StCode> to reach the Status Codes screen. Press <F1: Reset> to reset the unit's status condition for the next run to "OK."

A-4 Performance Test for Partisol 2300 Sampler

1.0 steps to be followed to verify sampler performance characteristics prior to starting a sampling run:

1.1 Ensure that cartridges are installed on the unit. Maintenance tasks and performance verification should be performed while in the Stop Mode. Press <MENU> to enter the Master Menu screen.

1.2 While in the Master Menu screen, press the down arrow (↓) until “Service Mode” is selected. Press <ENTER>. The unit then will display the Service Mode Confirmation screen.

1.3 Press <F3: Yes>. The unit will now display the Service Menu screen.

1.4 While in the Service Menu screen, press the down arrow (↓) until “System Maintenance Routines” is selected. Press <F2: SysChck>. The unit then will display the System Check screen.

1.5 While in the System Check screen, press <F1: Start>. The unit will automatically do a system check. When the system check has finished, press <ESC> to return to the Service Menu screen. While in the Service Menu screen, ensure that “System Maintenance Routines” is selected. Press <F1: Audit>. The unit then will display the Audit screen.

1.6 While in the Audit screen, verify the sampler’s ambient pressure by measuring the current ambient station pressure in mm Hg with an *external measurement device*. Verify that the value for ambient pressure displayed in the Audit screen is within ±10 mm Hg of the measured barometric pressure. If this is not the case, the sampler requires recalibration. Refer to the Service Manual.

1.7 Perform a leak check. While in the Audit screen, press <F4: LeakChk> to begin the leak check procedure.

1.8 The unit will prompt you to remove the cartridge that is on the flow channel which is being checked, and to install a leak plug on that flow channel. The flow channel that is being checked is identified under “Chnl” in the Audit screen. Install a leak plug on the proper channel.

1.9 After you have installed a leak plug on the proper flow channel, press any key on the keypad to begin the leak check. The unit will automatically perform a leak check. If a “Pass” message is displayed at the end of the leak check cycle, press <F2: + Chan> to switch the unit to the next flow channel. If a “Fail” message is displayed, refer to the Service Manual.

1.10 Re-install a cartridge on the flow channel that passed the leak check. Press <F4: LeakChk> to begin the leak check procedure on the next flow channel, and follow the instructions on the unit’s screen. Repeat the leak check procedure for all of the flow channels.

1.11 Verify the sampler’s flow. Ensure that the unit is set on the flow channel that you want to verify. Press <F5: Audit> and follow the instructions displayed on the unit’s screen. The unit will automatically verify the flow rate.

1.12 A “Pass” or “Fail” message will display at the end of the flow verification procedure. If a “Fail” message is displayed, refer to the Service Manual. If a “Pass” message is displayed at the end of the flow verification procedure, proceed to step 13.

1.13 Press <F2: + Chan> to switch the unit to the next flow channel. Press <F5: Audit> and follow the instructions displayed on the unit’s screen. Repeat the flow verification procedure for all of the flow channels.

A-5 Maintenance of Partisol 2300 Speciation Sampler

Routine Maintenance Procedures

1.0 Chemcomb Maintenance

O-Ring Maintenance
New ChemComb O-rings require a thin coating of silicon vacuum grease. Periodically re-grease the O-rings as needed.

Steps to be followed to apply grease to the O-rings:

1.1 Clean the O-rings with a moist tissue paper, if necessary.

1.2 Place a small amount of grease on end of your index finger and rub it onto the O-ring. Use your thumb and index finger to spread the grease until it covers the entire surface of the O-ring.

1.3 Wipe the excess grease from your fingers, and then use your cleaned fingers to rub any excess grease from O-rings.

2.0 Other Routine Maintenance

The routine maintenance of the Partisol Speciation Sampler consists of the following procedures performed at the indicated intervals:

Leak check: Perform a leak check after every 4 weeks of use.

Rain-hoods: Clean the air screens located under the sampler's rain-hoods every 6 months, or as necessary.

Batteries: Check the voltage level of the batteries on the main computer board in the electronics compartment every 6 months.

Pump: The pump in the Speciation Sampler has a lifetime of approximately 12-18 months. If the pump's performance deteriorates, it should be rebuilt using the Partisol Pump Rebuild Kit (59-007837) (two kits are required for each rebuild), or replaced with a new pump (RandP part number 54-006528-0120).

A-6 Leak Check of Partisol 2300

1.0 Steps to be followed to perform a leak check:

1.1 While in the Audit screen, press <F4: LeakChk> to begin the leak check procedure.

1.2 The unit will prompt you to remove the cartridge that is on the flow channel which is being checked, and to install a leak plug on that flow channel. The flow channel that is being checked is identified under “Chnl” in the Audit screen. Install a leak plug on the proper channel.

1.3 After you have installed a leak plug on the proper flow channel, press any key on the keypad to begin the leak check. The unit will automatically perform a leak check. If a “Pass” message is displayed at the end of the leak check cycle, press <F2: + Chan> to switch the unit to the next flow channel.

1.4 Re-install a cartridge on the flow channel that passed the leak check. Press <F4: LeakChk> to begin the leak check procedure on the next flow channel, and follow the instructions on the unit’s screen. Repeat the leak check procedure for all of the flow channels.

2.0 Verifying the Flow Rates

Perform the temperature verification, pressure verification and leak check before executing the flow verification procedure.

Steps to verify the flow rate:

2.1 Ensure that the unit is set on the flow channel that you want to verify. While in the Audit screen, press <F5: Start> and follow the instructions displayed on the unit’s screen. The unit will automatically verify the flow rate.

2.2 A “Pass” or “Fail” message will display at the end of the flow verification procedure. If a “Pass” message is displayed at the end of the flow verification procedure, proceed to step 3.

2.3 Press <F2: + Chan> to switch the unit to the next flow channel. Press <F5: Start> and follow the instructions displayed on the unit’s screen. Repeat the flow verification procedure for all of the flow channels.

Annexure-B: Filter sample preparation, handling and weighing

1.0 Scope

This procedure is applicable for weighing of Teflon Filter paper and Preconditioning of Quartz filter paper used for collecting PM_{10} and $PM_{2.5}$

2.0 Referred Documents

2.1 Weighing balance Operation Manual

2.2 Model Standard Operating Procedures (SOPs) For Sampling And Analysis by Central Pollution Commission Board, New Delhi

2.3 Furnace

3.0 Significance and Use

Pre-conditioned blank filter paper is weighed using weighing balance. The weighed filter paper is sent to the field for sampling. The filter paper which has undergone field sampling is received in the laboratory. The received filter paper is kept for conditioning. The conditioned field sample is again weighed using weighing balance and is used for further analysis.

4.0 Apparatus

The designated chemist, engineer will select the appropriate testing reforming master list of instruments.

4.1 Weighing balance (Make: Sartorius, Model: M5P, Mesh Type)
4.2 Teflon coated forceps
4.3 Millipore Petrislides
4.4 Cool kit
4.5 Filter Paper used for Sampling:
  4.5.1 Teflon Filter paper: 2 μm PTFE 47 mm filter with PP Ring supported (Whatman make)
  4.5.2 Quartz Filter paper: Tissuequartz 2500QAT-UP (Pall Make)

5.0 Procedure

5.1 Guidelines for Conditioning of Filter Papers:
Filter papers selected for different analytical objectives should be conditioned by following steps:

- Inspect all the filter papers for holes or cracks. Reject, if any deformity is found.
- Note down the batch/lot in log sheet.
- Label all the filters following a general lab coding technique, which should be unique to represent a sample.
- Put the marked filters in petri dishes.
- Use always proper (blunt) twizers/forceps (made of non-reactive material) to handle the filter papers in lab and field as well.
- Prepare a sample-tracking sheet for each filter paper or a batch of filter paper.

5.2 Filter Inspection and Stability
To equilibrate, the filters are transferred from their sealed manufacturer's packaging to a filter-handling container such as a plastic petri-slide. The filters are handled with non-serrated forceps. Lab personnel must wear vinyl gloves as secondary when filters are being prepared for conditioning and weighing. Before any filter is placed in a filter-handling container, it must be inspected for defects. This is done be an examination of the filter on

a "light table". A filter must be discarded if any defects are identified. Specific defects to look for are:

- Pinhole – A small hole appearing as a distinct and obvious bright point of light when examined over a light table.
- Separation of ring –Any separation or lack of seal between the filter and the filter support ring.
- Chaff or flashing – Any extra material on the reinforcing ring or on the heat-seal area that would prevent an airtight seal during sampling.
- Loose materials –Any extra loose materials or dirt particles on the filter.
- Discoloration –Any obvious discoloration that might be evidence of contamination.
- Other – A filter with any imperfection not described above, such as irregular surfaces or other results of poor workmanship.

6.0 Filter Conditioning

6.1 Pre-firing of Quartz-Fiber Filters

Quartz-fiber filters absorb organic vapors over time. Blank quartz-fiber filters should be heated for a lot at least three hours at 900°C. One sample of each batch of 100 pre-fired filters is tested for carbon blank levels prior to sampling, and sets of filters with carbon levels exceeding 1µg/cm^3 are re-fired or rejected. All pre-fired filters should be sealed and stored in a freezer prior to preparation for field sampling.

6.2 Weighing of Teflon-Membrane Filters before and after sampling

Gravimetric measurement is the net mass on a filter by weighing the filter before and after sampling with a balance in a temperature and relative humidity controlled environment as described in SOPs. To minimize particle volatilization and aerosol liquid water bias, PM2.5 reference methods require that filters be equilibrated for 24 hours at a constant (within ±5%) relative humidity between 30% and 40% and at a constant (within ±2ºC) temperature between 20ºC and 23ºC, which is a more stringent requirement than for PM10 filter equilibration. PM10 filters are required to be equilibrated at 20% to 45% relative humidity (±5%) and 15ºC to 30ºC temperature (±3ºC).

These filter equilibrium conditions are intended to minimize the liquid water associated with soluble compounds and to minimize the loss of volatile species. Nominal values of 30% RH and 20ºC best conserve the particle deposits during sample weighing. Accurate gravimetric analyses require the use of filters with low dielectric constants, high filter integrity, and inertness with respect to absorbing water vapor and other gases.

Annexure-C: Carbon Analysis

Analysis of Organic Carbon (OC) and Elemental Carbon (EC) in Particulate matter (PM_{10} and $PM_{2.5}$)

1.0 Scope

This procedure describes the analysis of exposed quartz micro fiber filters for organic carbon (OC) and elemental carbon (EC) in Particulate matter (PM) samples using a Desert Research Institute (DRI) Thermal/Optical Carbon Analyzer

2.0 Referred Documents

2.1 Standard Operating Procedure (SOP) MLD 065 Standard Operating Procedure for the analysis of Organic and Elemental Carbon in Particulate matter (PM) samples by using DRI Model 2001 TOR/TOT Carbon Analyzer.

2.2 Operation manual of DRI make Thermal/Optical Carbon Analyzer.

3.0 Summary of test Procedure

The operation of the DRI Model 2001 Thermal/Optical Carbon Analyzer is based on the preferential oxidation of organic carbon (OC) compounds and elemental carbon (EC) at different temperatures. The principal function of the optical (laser reflectance and transmittance) component of the analyzer is to correct for pyrolysis charring of OC compounds into EC. Without this correction, the OC fraction of the sample might be underestimated and the EC fraction might include some pyrolyzed OC.

4.0 Apparatus

The designated chemist, engineer will select the appropriate testing reforming master list of instruments.

4.1 Desert Research Institute (DRI) Model 2001A Thermal Optical Carbon Analyzer (AML/ INST/ 149) System with computer.
4.2 Stainless steel punching tool: 5/16-inch diameter, 0.5 cm2 nominal area.
4.3 Syringes: Hamilton Gas-Tight 1000 µl syringe for calibration injections; 25 µl syringe for carbonate analysis and for analyzer calibration.
4.4 Flat-tip tweezers.
4.5 Flat glass plate.
4.6 Tissue paper
4.7 Glassware

4.8 Gases: All gases are required of high purity grade

Sr. No.	Name of the gas	Regulated pressure (psi)	Purpose
1	Helium	15-40	As a carrier gas
2	10 % O_2 in helium	15	As a carrier gas
3	Hydrogen	15	As a fuel for FID
4	Zero air	15	As an Oxidiser for FID
5	Zero air	~25	For pneumatic activation
6	5% methane in He	10	Internal Calibration
7	5% CO_2 in He	10	Calibration

5.0 Chemicals:

5.1 Potassium Hydrogen Phthalate (KHP)
5.2 Sucrose
5.3 Hydrochloric Acid (HCl)
5.4 Ultrapure ASTM type 1 deionized water (>16 Mega Ohm-cm).

6.0 Procedure

6.1 Analyzer start-up (When the analyzer is started up for the first time, or after an extended period of non-operation):

- Check the gases for their pressures/settings.
- Start all the gases except Air to FID on front panel
- Start PC only.
- Put on Analyzer (Switch is on the rear side of the analyzer.)
- Set FID temperature to 125^{o}C and Line Heater temperature to 105^{o}C.
- Heat Both Oxygenator to 912^{o}C and Methanator to 425^{o}C with an increment of 100^{o}C withhold time 30 minutes at each increment.
- It will take a period of three days for conditioning to reach a stable system background.
- When system stabilization is achieved then perform the leak check test. For daily routine operation, start the operation with leak check test onwards.

6.2 Leak Check test

- Close sample oven outlet toggle valve on right side of control panel.
- Wait for sample oven pressure display to reach approximately 5 units from 2.6 units.
- Then close sample oven inlet valve on the front panel.
- A “leak free” condition is indicated by a steady pressure reading, or a decline of 0.01 units or less per second
- After the leak check test is PASS, then open sample oven outlet valve and then open the sample oven inlet.
- Click the DriCarb shortcut icon from desktop to begin the carbon program
- Make sure that the analyzer’s multi-function switch (at the left of the front panel) is at auto mode on front panel.

6.3 Oven Baking

- Oven Baking is performed after Leak Check is passed
- Select “Analysis” from the “Main” submenu of the Welcome form. This will initiate the analysis protocol.
- Under “Command Table”, select *cmdlBakeOven*.
- In the analysis “Setup” form, enter “Sample” for the Type.
- Enter the Sample ID number as “OB1”, Enter the Run #, Punch area and Deposit area for the filter being analyzed. Punch area and Deposit area should be “1”. Enter technician initials in the “Tech initials” field.
- Click “OK” on the analysis “Setup” screen.
- Repeat until the system is clean. Sample runs or calibrations may then begin.
- System blanks are run after the oven bake.

6.4 System Blank

- System blanks are run at the beginning of each day after oven baking.
- Run a system blank with the IMPROVE_A protocol.
- Select “Analysis” from the “Main” submenu of the Welcome form. This will initiate the analysis protocol.
- n the analysis “Setup” form, enter “Sample” for the Type. Select FID ID as FID_8

- Polarity should default to "Unipolar". Fill out the information about the sample, including: Project Name as SysBlk, Batch #, and Subbatch#.
- Under "Command Table" select *cmdImproveA*.
- Enter the Sample ID number as SysBlank_date, Enter the Run #, Punch area and Deposit area for the filter being analyzed. Punch area and Deposit area should be "1". Enter technician initials in the "Tech initials" field.
- Select any pre-analysis flags from the drop-down menu in the "Flags" field.
- Click "OK" on the analysis "Setup" screen. Computer will prompt to load the filter punch. But when prompted to load filter punch, remove the filter from the previous day and leave the boat empty. Enter delay value as 10 sec. Click "OK"
- The boat will load to the calibration position after 10 sec. The computer will ask, "Would you like to proceed or would you like to delay analysis?" Enter a 130-second delay is in the "delay" box. Click "OK" and analysis will begin.
- Calculated carbon concentrations should not be more than 0.2 µg carbon. Values greater than this warrant additional system blanks. Samples may not be analyzed until the system blank is <0.2 µg carbon. After this carry out filter-blank analysis.

6.5 Auto-calibration

- Auto-calibration is performed after system blank
- Select "Analysis" from the "Main" submenu of the Welcome form. This will initiate the analysis protocol.
- Under "Command Table" select *cmdlAutoCalibcheck*.
- In the analysis "Setup" form, enter "Sample" for the Type.
- Enter the Sample ID number as "AutoCalib_Date", Enter the Run #, Punch area and Deposit area for the filter being analyzed. Punch area and Deposit area should be "1". Enter technician initials in the "Tech initials" field.
- Click "OK" on the analysis "Setup" screen.
- After the run time is over, computer will prompt the calibration check result.
- Do not proceed to sample analysis unless calibration is established or confirmed. There should not be more than 10% difference in three peak areas of calibration.

6.6 Sample analysis

- Note down the sample details.
- Examine the filter visually and note any non-uniformity or unusual deposit. Place the filter on the flat glass plate and remove a sample punch using punching tool.
- Select "Analysis" from the "Main" submenu of the Welcome form. This will initiate the analysis protocol.
- In the analysis "Setup" form, enter "Sample" for the Type. Select FID ID as FID_8
- Polarity should default to "Unipolar". Fill out the information about the sample, including: Project Name as SysBlk, Batch #, and Subbatch#.
- Under "Command Table" select *cmdImprove*.
- Enter the Sample ID number, Enter the Run #, Punch area and Deposit area for the filter being analyzed. Enter technician initials in the "Tech initials" field.
- Select any pre-analysis flags from the drop-down menu in the "Flags" field.
- Click "OK" on the analysis "Setup" screen. Computer will prompt to load the filter punch. But when prompted to load filter punch, remove the filter from the previous day and leave the boat empty. Enter delay value as 10 sec. Click "OK"
- The boat will load to the calibration position after 10 sec. The computer will ask, "Would you like to proceed or would you like to delay analysis?" Enter a 130-second delay is in the "delay" box. Click "OK" and analysis will begin. Report of analysis will be generated automatically.

6.7 Filter blank

- Filter blank analysis, one for every 10 samples analysed, is performed similar to sample analysis with pre-baked blank filter paper punch loaded instead of sample punch.
- Pre-baking of blank filter paper is carried out by heating the blank filter paper in furnace at 900°C for 4 hrs using porcelain dishes and preserved in dessicator.

6.8 Calibration

- The instrument is calibrated every six months or the internal calibration gas cylinder is changed, whichever is earlier. 5% CO_2 in He, 5% CH_4 in He and KHP are used for calibration. 5% CH_4 in He is also used for end of run calibration automatically injected by the instrument.
- 5% CO_2 in He is injected in the volume 100 ul, 200 ul, 500 ul, 700 ul and 1000 ul.
- 5% CH_4 in He is injected in the volume 100 ul, 200 ul, 500 ul, 700 ul and 1000 ul.
- KHP solution of 1800 ppm concentration is used for calibration. Following volumes were injected- 5 ul, 10 ul, 15 ul and 20 ul, which corresponds to 9 ug, 18 ug, 27 ug and 36 ug Carbon.
- The gas standard concentrations are corrected for temperature and pressure at laboratory conditions using ideal gas law and certified percent of gas in cylinder.
- The injection peak counts divided by calibration peak counts is calculated and slope is determined by plotting calculated carbon in ug vs. injection peak area/calibration peak area. The line is forced through zero.
- The slope value determined from three calibration standards is entered into *carbon.par* table

7.0 Calculations

The conversion of integrated peak counts to µg of carbon for each peak in the thermogram is performed by the computer at the end of the analysis program based on analysis result, punch area, deposit area, internal calibration peak area.

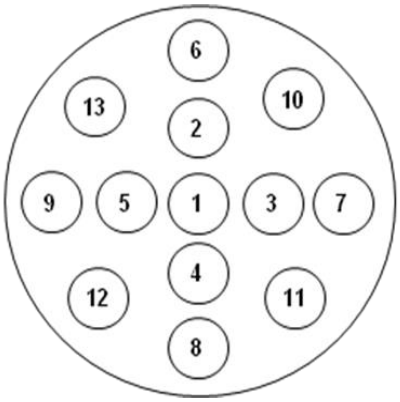
Carbon Fractions	Temperature Range
OC1	25^0C -140^0C
OC2	140^0C -280^0C
OC3	280^0C -480^0C
OC4	480^0C -580^0C
EC1	580^0C
EC2	580^0C -780^0C
EC3	780^0C -840^0C

8.0 Reporting

Report Concentration of Organic carbon fractions (OC1, OC2, OC3 and OC4) and Elemental Carbon Fractions (EC1, EC2 and EC3) in the PM.

9.0 Calibration Records

Table C-1: Carbon analysis at various locations of PM collected on Quartz Filter paper



μg of Carbon on filter paper

Sr. No.	Sample ID	VOC	Regular OC	High Temp OC	Regular EC	High Temp EC	TC
1	Quartz Paper 1 – Punch 1	1.29	444.18	442.89	357.81	56.18	801.99
2	Quartz Paper 1 – Punch 2	1.28	407.25	405.97	325.05	34.43	732.29
3	Quartz Paper 1 – Punch 3	4.70	397.81	393.11	315.37	32.72	713.18
4	Quartz Paper 1 – Punch 4	0.67	397.69	397.03	281.57	42.21	679.26
5	Quartz Paper 1 – Punch 5	0.53	426.64	426.11	348.88	76.37	775.52
6	Quartz Paper 1 – Punch 6	0.52	357.93	357.41	269.03	49.31	626.96
7	Quartz Paper 1 – Punch 7	0.81	398.13	397.32	323.66	50.80	721.78
8	Quartz Paper 1 – Punch 8	1.10	345.68	344.57	307.93	51.46	653.61
9	Quartz Paper 1 – Punch 9	0.93	428.67	427.75	352.18	59.26	780.86
10	Quartz Paper 1 – Punch 10	0.87	399.91	399.04	329.55	35.92	729.46
11	Quartz Paper 1 – Punch 11	0.91	453.16	452.24	346.17	47.88	799.32
12	Quartz Paper 1 – Punch 12	0.95	445.68	444.73	355.90	39.63	801.57
13	Quartz Paper 1 – Punch 13	0.91	405.32	404.41	335.81	49.79	741.13
Average		1.19	408.31	407.12	326.84	48.15	735.15
Standard Deviation		1.08	32.03	32.10	27.82	11.87	56.96

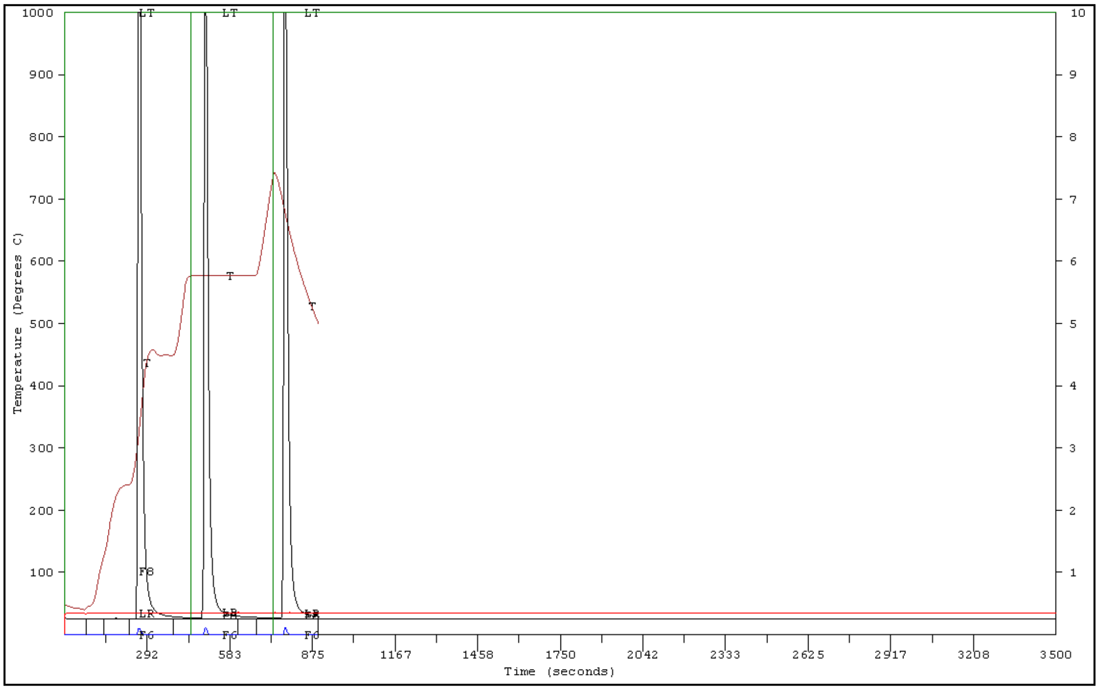


Fig. C-1: Typical example of Auto-calibration run taken on every day before actual testing starts

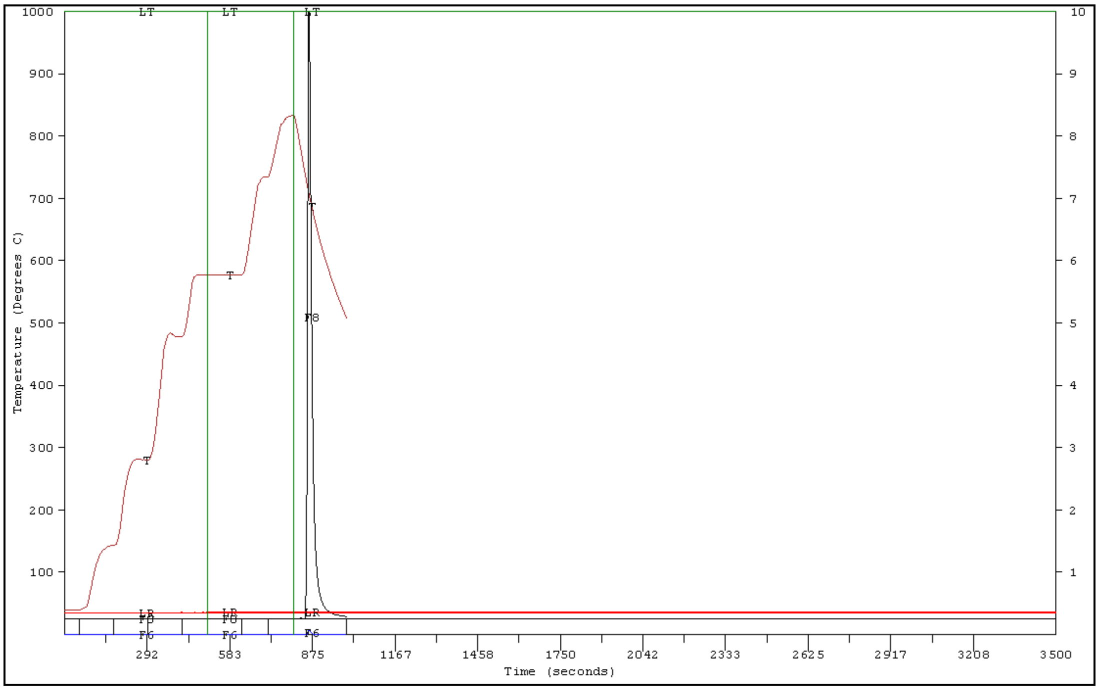


Fig. C-2: Typical example of System Blank run taken on every day before actual testing starts

Annexure-D: Analysis of Ions

Method for measurement of Anions and Cations in Particulate matter (PM) samples by Ion Chromatography

1.0 Scope

Method for measurement of Anions and Cations in Particulate matter (PM) samples by Ion Chromatography

2.0 Reference Document

2.1 Standard Operating Procedure (SOP) MLD 064 Standard Operating Procedure for the analysis of anions and cations in $PM_{2.5}$ speciation samples by Ion Chromatography.

2.2 Operation manual of Metrohm make Ion Chromatograph.

2.3 Methods of Air Sampling and Analysis, 3rd Edition by James p. Lodger

2.4 Refer file No. CHL/MSDS/74 for Applicable MSDS for proper handing storage use disposal of chemicals for --

- Sodium Carbonate (Na_2CO_3)
- Sodium Bi-Carbonate ($NaHCO_3$)
- Tartaric Acid
- Pyridine 2,6 Di-Carboxylic Acid or Dipicolinic Acid

3.0 Summary of Test Procedure

The method determines the anions and cations present in PM e.g. PM10 / PM2.5 dust collected on Teflon filter papers from ambient air which are collected from different sites. The filters are extracted in deionized water by sonicating for one hour, and filtered through 0.2-micron membrane filters. Ion Chromatography using a system comprising of guard column, analytical column, self-regenerating suppressor and a conductivity detector analyzes the final extract. The peak analysis is determined by using Metro data IC Net Software Version 2.3

- Ions analysd by Ion chromatohraph:
  - Cation : Na^+,K^+,Mg^+,NH_4^+,Ca^{++}
  - Anion: Cl-,F-,Br-,NO_3^-,SO_4^{--}

4.0 Apparatus:

The test procedure assumes Metrohm Ion Chromatographic system. For detailed instructions in the operation of the Metrohm IC refer to the operation manual of Metrohm.

4.1 Metrohm Ion Chromatographic system comprised of following modular units, one for Anions and one for Cations:

- Isocratic pump
- IC interface (shared by both anions and cations)
- Separation Center
- Suppressor Module
- Conductivity detector
- Automated Sampler

4.2 IC Operating Conditions:

Sample loop volume:	20 µl for anions and cations
Analytical Column: Anions Cations	 Metrosep A Supp 5 250 Metrosep C2 250
Guard Column: Anions Cations	 Metrosep A Supp 5 250,Guard Metrosep C2 250,Guard
Eluent solutions: Anions	 3.2mM carbonate / 1.0 mM bicarbonate
Eluent solutions: Cations	4 mM Tartaric Acid / 0.75mM Dipicolinic Acid or 2,6 Pyridine Dicarboxylic Acid
Eluent flow rates: Anions Cations	 0.70ml/min 1.0ml/min
Acquisition Software	Metro data IC Net Software Version 2.3
Pressure	Max. 15MPa
Suppressor	Regenerating agent 50mmol/L H_2SO_4
Analysis Time: Anion Cation	 35min 37min

4.3 Other Equipment:

- Ultrasonicator
- Analytical balance
- Vacuum Filtration System

4.4 Glassware:

- Volumetric flasks: 10,250,500 and 1000 ml sizes
- Polyethylene storage bottles
- Beakers: 25,50,100 ml sizes
- Metrohm Autosampler 10ml Vials with caps
- Pipettes : 1,5 and 10 ml
- Gloves disposable

5.0 Reagents:

- Sodium Carbonate (Na_2CO_3)
- Sodium Bi-Carbonate ($NaHCO_3$)
- Oxalic Acid
- Sulphuric acid (H_2SO_4)
- Pyridine 2,6 Di-Carboxylic Acid or Dipicolinic Acid
- ASTM type 1 deionized water (>16 Mega Ohm-cm)
- Anion Mix Standard (Cl^-,F^-,Br^-,NO_3^-,SO_4^{--}) 10 ppm concentration (Certified Multielement Ion Chromatography Anion Standard Solution) SIGMA-ALDRICH Make Cation Mix Standard (Na+,K+,Mg+,NH_4+,Ca+) 10 ppm concentration(Certified Multielement Ion Chromatography Cation Standard Solution) SIGMA-ALDRICH Make

6.0 Procedure:

Preparation of Eluents-
Stock eluents are prepared in ultrapure water. The following table lists the amounts of each chemical used to make one batch of stock solution:

Eluent	Stock Eluent	Amount per batch
Anion Eluent	Sodium carbonate and Sodium bicarbonate	3.2mM (0.1696gm/500ml) and 1.0 mM (0.0420 gm/500ml)
	Sulphuric Acid Regenerant	50mMol (1.33ml / 500ml)
	Ultrapure Water	Type 1 grade 250ml
Cation Eluent	Tartaric Acid and Dipicolinic Acid or 2,6 Pyridine-Dicarboxylic Acid	4 mM (0.600gms/lit) and 0.75mM (0.125gm /lit)

6.1 Anion Eluent – Weigh the Sodium carbonate and Sodium bicarbonate as per quantity given in above table and transfer into a 500ml volumetric flask. Add approximately 150 ml of ultrapure water and stir the contents till their dissolution in water. Once all chemicals have dissolved make the volume to 500 ml with ultrapure water. Filter this solution with 0.2μ-size membrane filter using vacuum filtration system. Now the solution is ready for use. Always use clean and oven dried glassware for eluent preparation. The reagents should be prepared in ultrapure water and filtered through 0.2μ size membrane filter.

6.2 Sulphuric Acid Regenerant – Pipette out the conc. H_2SO_4 (AR grade 98% pure) with clean and oven dried pipette. Transfer it into 500 ml volumetric flask and make up the volume with ultrapure water. Follow the same procedure for filtration as for anion eluent preparation.

6.3 Cation Eluent – Weigh the Tartaric Acid and Dipicolinic Acid or 2,6 Pyridine Dicarboxylic Acid and transfer into a 1lit size volumetric flask. Add approximately 150 ml of ultrapure water and stir the contents till their dissolution in water. Once all chemicals have dissolved make the volume to 1000 ml with ultrapure water. Follow the same procedure for filtration as for anion eluent preparation

6.4 Preparation of Anion and Cation Calibration Standards

The anion and cation standard are both of 10 mg/lit (10μg/ml) concentrations. The standards are stored in the refrigerator until their use. For three-point calibration varying range of concentrations of 1ppm, 5ppm and 10 ppm are prepared from stock of 10 ppm. All the dilutions are made in ultrapure deionized water. The working standards are usable for no more than a month before they must be prepared again from stock standard solution. The report of three-point calibration for both anions and cations are enclosed.

6.5 Filter Analysis:

Filter papers are stored in a controlled temperature and humidity conditions. Following steps were followed before taking samples for analysis:

- Prepare a work list of samples to be analyzed containing details of date of collection of sample, site identification, duration of sample collection and any other observations interfering the analysis.
- Label the samples properly with above details and should be numbered.
- Always consider one field blank and one laboratory blank for each set of samples.
- Prepare sequence for the analytical run that begins with the calibration standards in order of increasing concentration, followed by water blank and sample. Follow this list including at least 10 % duplicate and after each set of analysis another check standard. At the end of the samples field blank and laboratory blank are analyzed.
- Cut the exposed filter into small pieces with cutter and place it in a 50 ml beaker. Add 30 ml deionized water into it. Also take one blank filter (unexposed to air) and follow same procedure.
- Place all the beakers in ultrasonicator bath for 60 min. After sonication remove them from bath and wipe the bottom of beaker with towel or tissue paper.
- After sonication shake the samples and stir the contents in the beaker.

- Filter the samples now through 0.20-micron size membrane (Pall Gelman make or equivalent) filters using vacuum extraction assembly. Ensure that the extract is clear and transparent after filtration. Make up the volume of sample up to 50 to 100 ml depending upon the analysis requirement. If concentration of an analyte is beyond the range of calibration, dilute the sample accordingly. The sample is now ready for analysis on Ion Chromatograph.
- Transfer the contents of sample into autosampler vials and cap each vial .Run the sequence of samples as mentioned above and operate the IC Net Software for simultaneous analysis of anions and cations at above instrumental conditions. The results are given in ppm or mg / lit.

7.0 Calculations:

7.1 Calculation of Volume of Air Sampled

V = QT
V = Volume of air sampled in m^3
Q = Average flow rate in m^3/minute
T = Total sampling time in minute

7.2 Calculation of Anions and Cations in PM in Ambient Air

Concentration of Ion $\mu g/ m^3$ = $[(C \times V_1) - B] / (V \times F)$

Where,
C= concentration of (µg or mg of Ion / ml) in the aliquot
V_1 = Volume of aliquot (ml)
B = total µg or mg of Ion in blank
F = Fraction of total sample in the aliquot used for measurement
V = Volume of air sampled

8.0 Report

Report Concentration of desired anions and cations in mg and percentage (%) and micrograms (µg) per cubic metre (m^3) of ambient particulate matter.

9.0 Calibration Records:

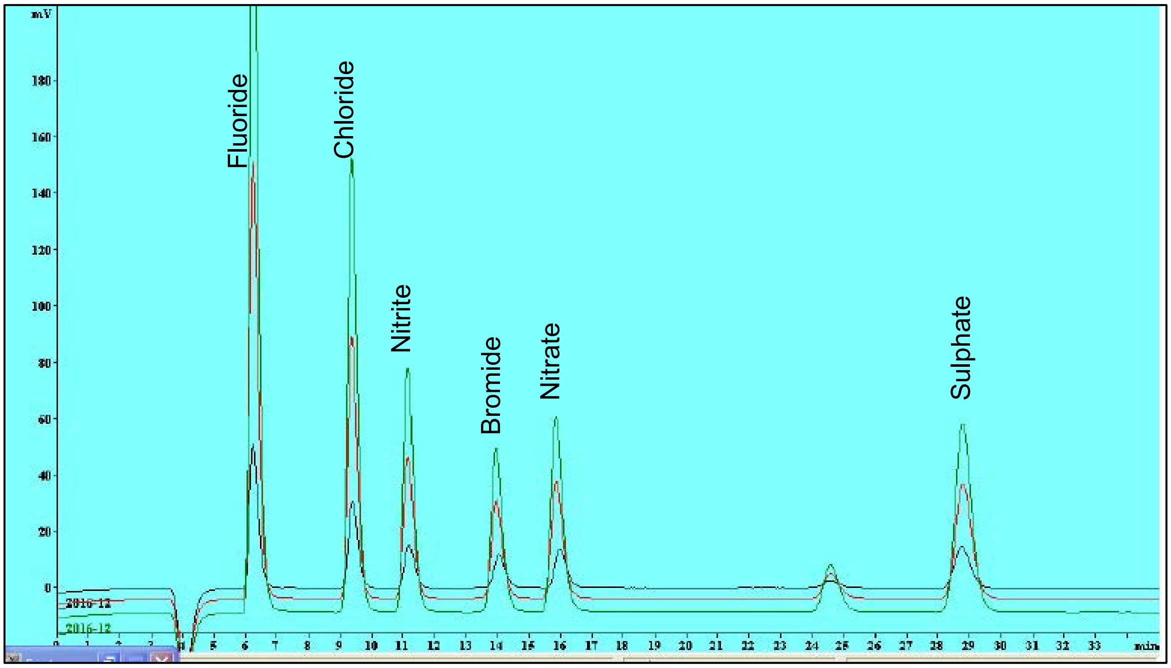


Figure D-1: Overlay of Calibration Run of 1 ppm, 3 ppm and 5 ppm run of Anion

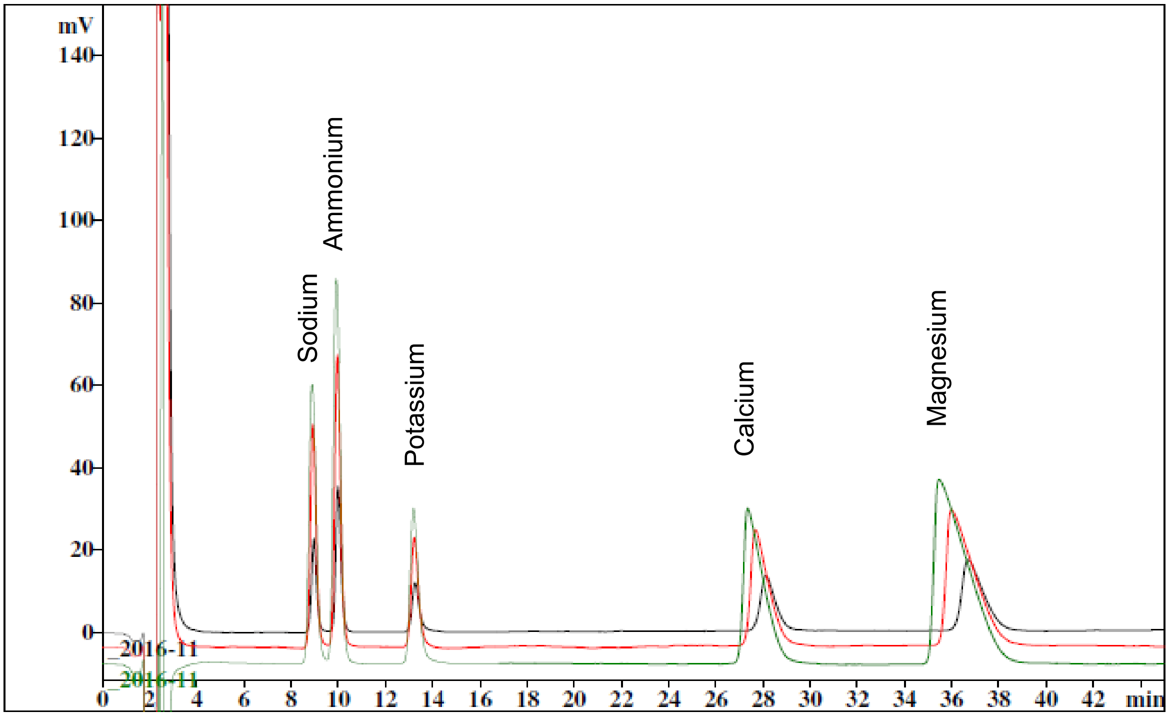
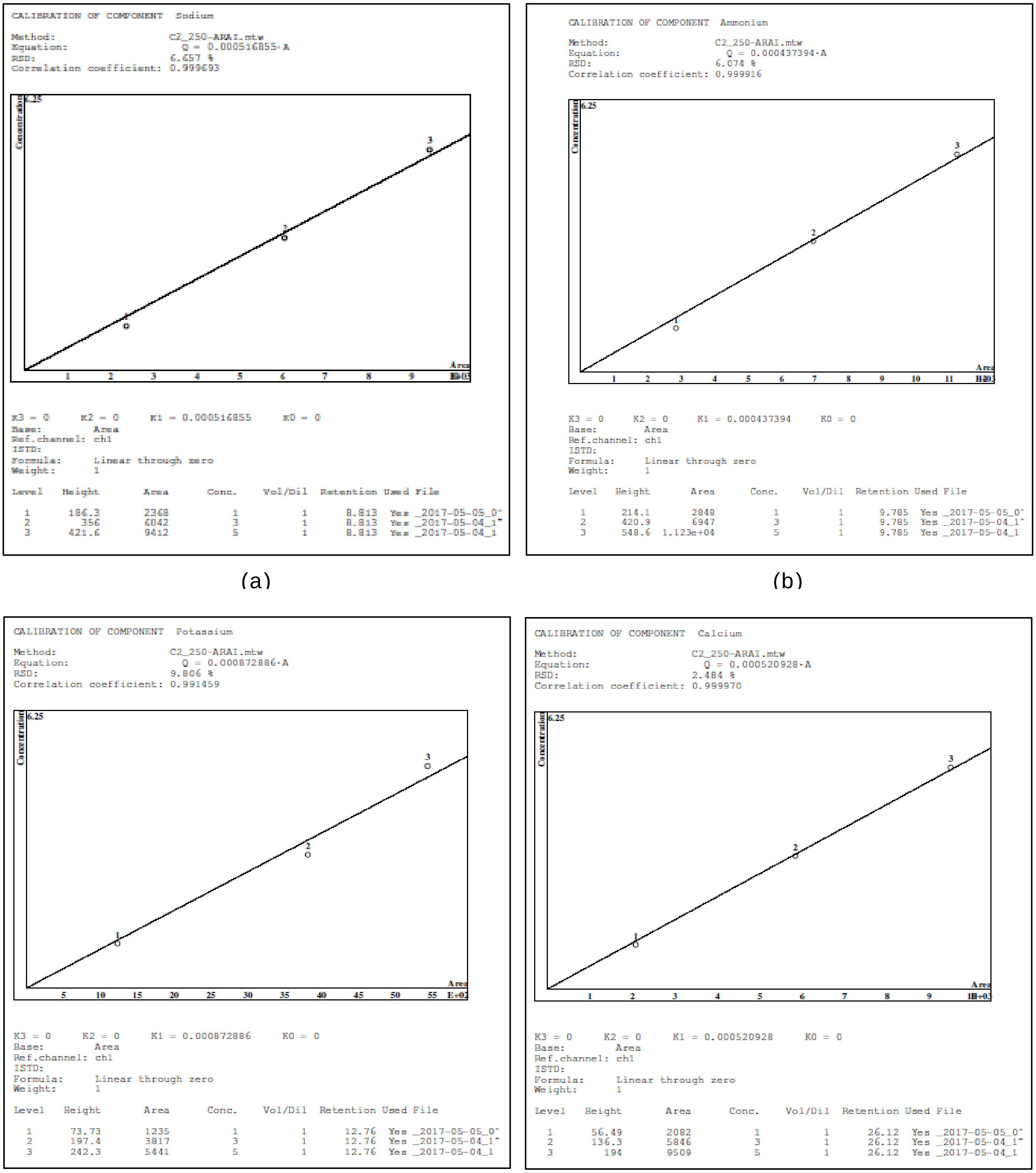


Figure D-2: Overlay of Calibration Run of 1 ppm, 3 ppm and 5 ppm run of Cation



```
CALIBRATION OF COMPONENT  Sodium

Method:                    C2_250-ARAI.mtw
Equation:                    Q = 0.000516855·A
RSD:                       6.657 %
Correlation coefficient:  0.999693

K3 = 0      K2 = 0      K1 = 0.000516855      K0 = 0
Base:          Area
Ref.channel:  ch1
ISTD:
Formula:       Linear through zero
Weight:        1

Level    Height        Area       Conc.     Vol/Dil  Retention Used File

  1       186.3        2368          1           1       8.813   Yes _2017-05-05_0"
  2         356        6042          3           1       8.813   Yes _2017-05-04_1"
  3       421.6        9412          5           1       8.813   Yes _2017-05-04_1
```

(a)

```
CALIBRATION OF COMPONENT  Ammonium

Method:                    C2_250-ARAI.mtw
Equation:                    Q = 0.000437394·A
RSD:                       6.074 %
Correlation coefficient:  0.999916

K3 = 0      K2 = 0      K1 = 0.000437394      K0 = 0
Base:          Area
Ref.channel:  ch1
ISTD:
Formula:       Linear through zero
Weight:        1

Level    Height        Area       Conc.     Vol/Dil  Retention Used File

  1       214.1        2848          1           1       9.785   Yes _2017-05-05_0"
  2       420.9        6947          3           1       9.785   Yes _2017-05-04_1"
  3       548.6   1.123e+04          5           1       9.785   Yes _2017-05-04_1
```

(b)

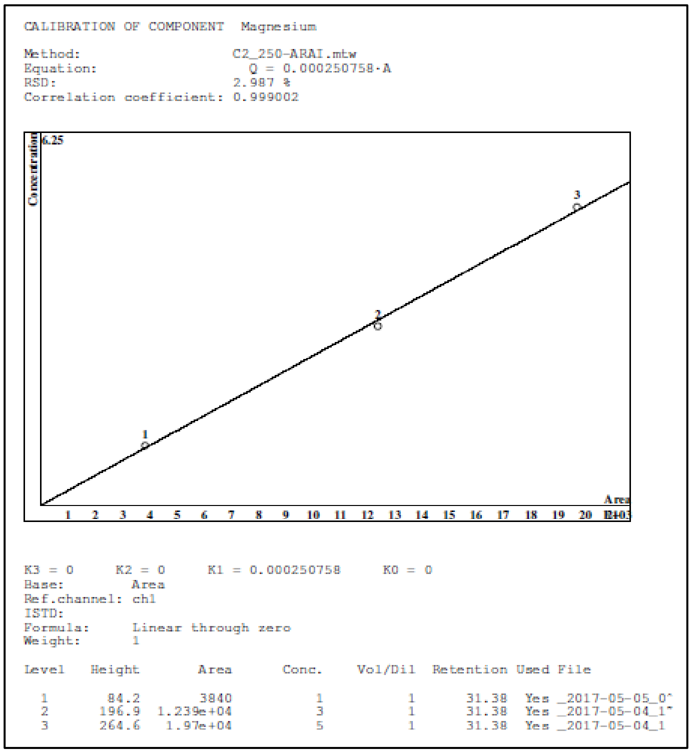
```
CALIBRATION OF COMPONENT  Potassium

Method:                    C2_250-ARAI.mtw
Equation:                    Q = 0.000872886·A
RSD:                       9.806 %
Correlation coefficient:  0.991459

K3 = 0      K2 = 0      K1 = 0.000872886      K0 = 0
Base:          Area
Ref.channel:  ch1
ISTD:
Formula:       Linear through zero
Weight:        1

Level    Height        Area       Conc.     Vol/Dil  Retention Used File

  1       73.73        1235          1           1       12.76   Yes _2017-05-05_0"
  2       197.4        3817          3           1       12.76   Yes _2017-05-04_1"
  3       242.3        5441          5           1       12.76   Yes _2017-05-04_1
```

(c)

```
CALIBRATION OF COMPONENT  Calcium

Method:                    C2_250-ARAI.mtw
Equation:                    Q = 0.000520928·A
RSD:                       2.484 %
Correlation coefficient:  0.999970

K3 = 0      K2 = 0      K1 = 0.000520928      K0 = 0
Base:          Area
Ref.channel:  ch1
ISTD:
Formula:       Linear through zero
Weight:        1

Level    Height        Area       Conc.     Vol/Dil  Retention Used File

  1       56.49        2082          1           1       26.12   Yes _2017-05-05_0"
  2       136.3        5846          3           1       26.12   Yes _2017-05-04_1"
  3         194        9509          5           1       26.12   Yes _2017-05-04_1
```

(d)

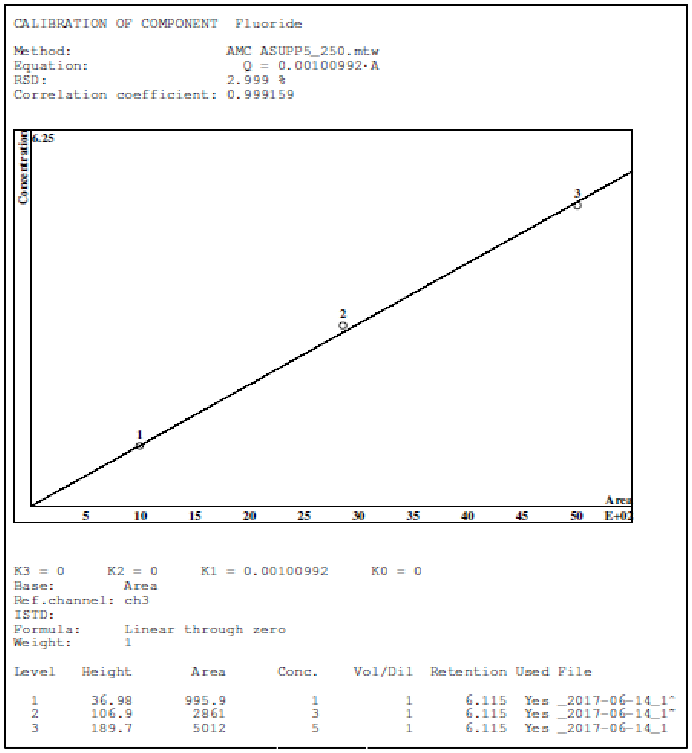
Figure D-3: Calibration Run linearity graph of 1 ppm, 3 ppm and 5 ppm run of Cation:
(a) Sodium (b) Ammonium (c) Potassium (d) Calcium (Representative graph for respective ion)



```
CALIBRATION OF COMPONENT  Magnesium

Method:                    C2_250-ARAI.mtw
Equation:                    Q = 0.000250758·A
RSD:                       2.987 %
Correlation coefficient:   0.999002
```

```
K3 = 0     K2 = 0     K1 = 0.000250758     K0 = 0
Base:          Area
Ref.channel:   ch1
ISTD:
Formula:       Linear through zero
Weight:        1

Level   Height       Area      Conc.    Vol/Dil  Retention Used File

  1       84.2       3840         1         1       31.38  Yes _2017-05-05_0
  2      196.9  1.239e+04         3         1       31.38  Yes _2017-05-04_1
  3      264.6   1.97e+04         5         1       31.38  Yes _2017-05-04_1
```

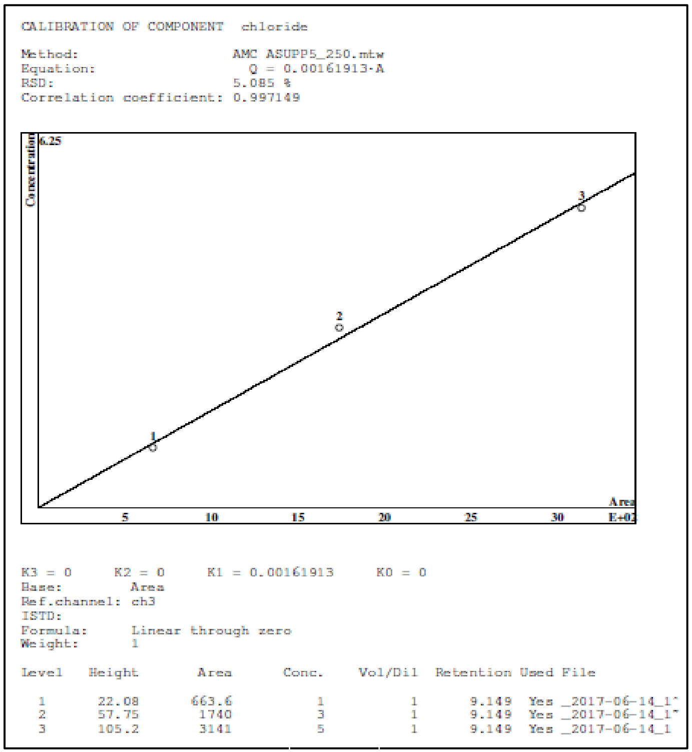
Figure D-4: Calibration Run linearity graph of 1 ppm, 3 ppm and 5 ppm run of Cation: Magnesium (Representative graph)



```
CALIBRATION OF COMPONENT  Fluoride

Method:                      AMC ASUPP5_250.mtw
Equation:                      Q = 0.00100992·A
RSD:                         2.999 %
Correlation coefficient: 0.999159
```

```
K3 = 0      K2 = 0      K1 = 0.00100992      K0 = 0
Base:            Area
Ref.channel: ch3
ISTD:
Formula:         Linear through zero
Weight:          1

Level    Height        Area        Conc.     Vol/Dil  Retention Used File

  1       36.98        995.9          1           1       6.115  Yes _2017-06-14_1
  2       106.9         2861          3           1       6.115  Yes _2017-06-14_1
  3       189.7         5012          5           1       6.115  Yes _2017-06-14_1
```

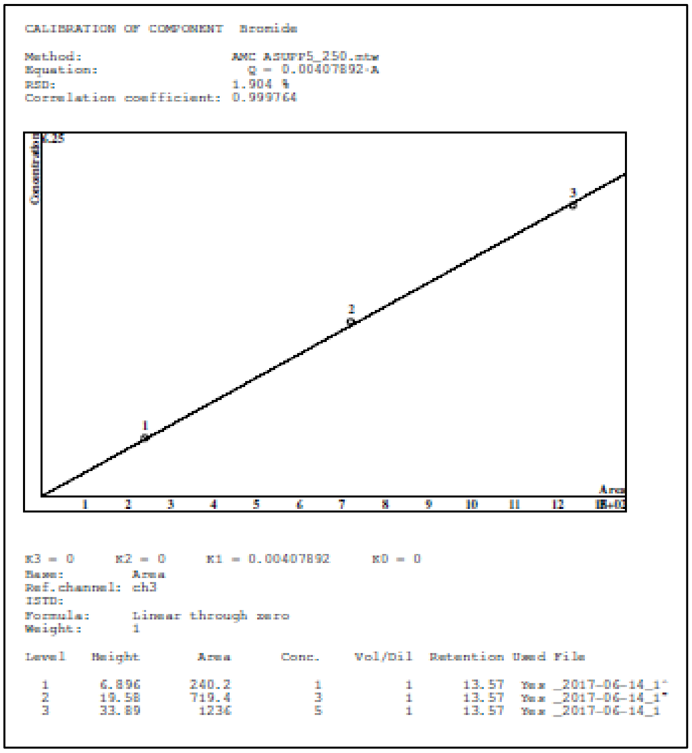
(a)



```
CALIBRATION OF COMPONENT  chloride

Method:                      AMC ASUPP5_250.mtw
Equation:                      Q = 0.00161913·A
RSD:                         5.085 %
Correlation coefficient: 0.997149
```

```
K3 = 0      K2 = 0      K1 = 0.00161913      K0 = 0
Base:            Area
Ref.channel: ch3
ISTD:
Formula:         Linear through zero
Weight:          1

Level    Height        Area        Conc.     Vol/Dil  Retention Used File

  1       22.08        663.6          1           1       9.149  Yes _2017-06-14_1
  2       57.75         1740          3           1       9.149  Yes _2017-06-14_1
  3       105.2         3141          5           1       9.149  Yes _2017-06-14_1
```

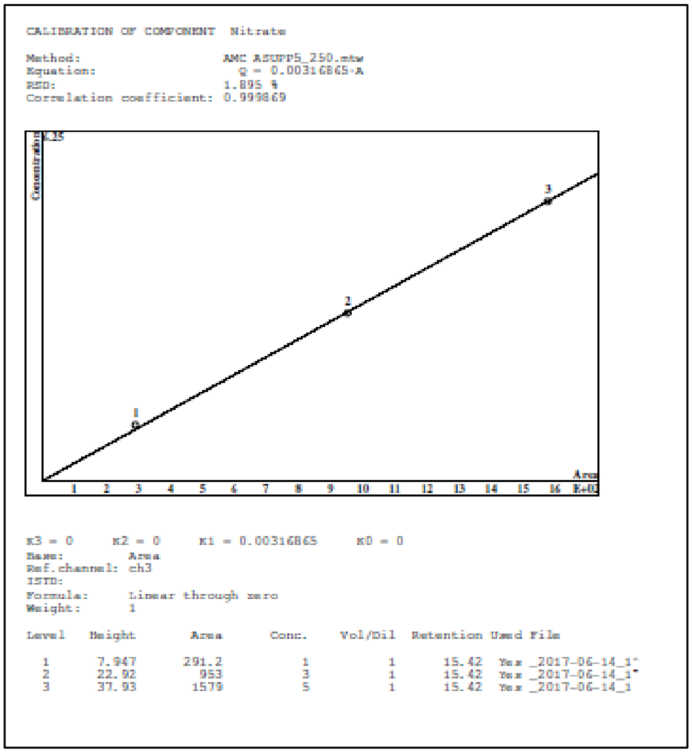
(b)



```
CALIBRATION OF COMPONENT  Bromide

Method:                      AMC ASUPP5_250.mtw
Equation:                      Q = 0.00407892·A
RSD:                         1.904 %
Correlation coefficient: 0.999764
```

```
K3 = 0      K2 = 0      K1 = 0.00407892      K0 = 0
Base:            Area
Ref.channel: ch3
ISTD:
Formula:         Linear through zero
Weight:          1

Level    Height        Area        Conc.     Vol/Dil  Retention Used File

  1       6.896        240.2          1           1       13.57  Yes _2017-06-14_1
  2       19.58        719.4          3           1       13.57  Yes _2017-06-14_1
  3       33.89         1236          5           1       13.57  Yes _2017-06-14_1
```

(c)

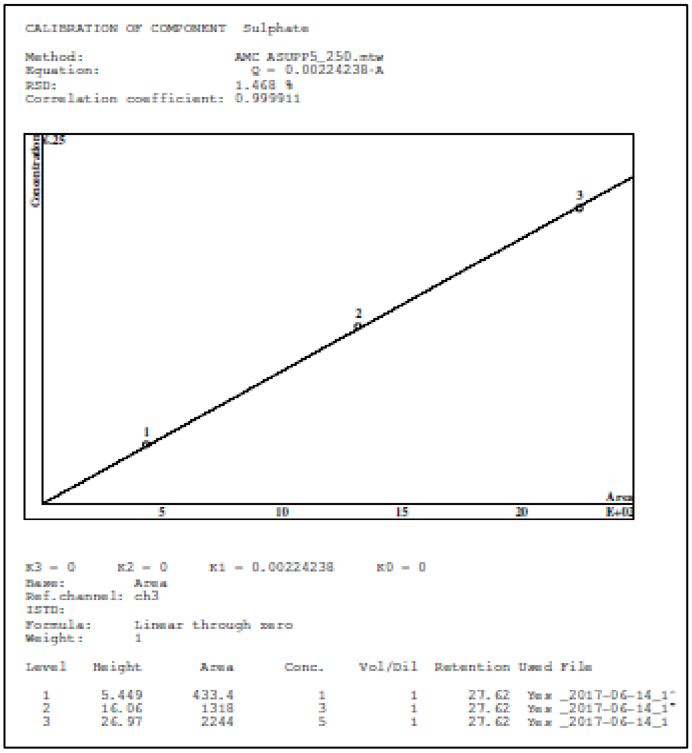


```
CALIBRATION OF COMPONENT  Nitrate

Method:                      AMC ASUPP5_250.mtw
Equation:                      Q = 0.00316865·A
RSD:                         1.895 %
Correlation coefficient: 0.999869
```

```
K3 = 0      K2 = 0      K1 = 0.00316865      K0 = 0
Base:            Area
Ref.channel: ch3
ISTD:
Formula:         Linear through zero
Weight:          1

Level    Height        Area        Conc.     Vol/Dil  Retention Used File

  1       7.947        291.2          1           1       15.42  Yes _2017-06-14_1
  2       22.92          953          3           1       15.42  Yes _2017-06-14_1
  3       37.93         1579          5           1       15.42  Yes _2017-06-14_1
```

(d)

Figure D-5: Calibration Run linearity graph of 1 ppm, 3 ppm and 5 ppm run of Cation: (a) Fluoride (b) Chloride (c) Bromide (d) Nitrate (Representative graph for respective ion)



```
CALIBRATION OF COMPONENT  Sulphate

Method:                  AMC ASUPP5_250.mtw
Equation:                  Q = 0.00224238·A
RSD:                     1.468 %
Correlation coefficient: 0.999911
```

```
K3 = 0     K2 = 0     K1 = 0.00224238     K0 = 0
Base:          Area
Ref.channel:  ch3
ISTD:
Formula:       Linear through zero
Weight:        1

Level   Height      Area      Conc.    Vol/Dil  Retention Used File

  1      5.449     433.4        1         1       27. 62   Yes _2017-06-14_1"
  2      16. 06     1318        3         1       27. 62   Yes _2017-06-14_1"
  3      26. 97     2244        5         1       27. 62   Yes _2017-06-14_1
```

Figure D-6: Calibration Run linearity graph of 1 ppm, 3 ppm and 5 ppm run of Cation: Sulphate (Representative graph)

Annexure-E: Analysis of Elements

Determination of Metal Content in Particulate Matter (PM) Collected On Teflon Filter Paper by X-Ray Fluorescence Spectrometer

1.0 Scope

1.1 This procedure is applicable to analysis of particulate matter (PM) collected on Teflon filter papers from ambient air.

2.0 Reference Document

2.1 Compendium Method IO-3.3, Determination of metals in ambient particulate matter using X-Ray Fluorescence (XRF) Spectroscopy, US EPA, June 1999

2.2 Panalytical Software manual.

3.0 Summary of Test Procedure

Elemental Analysis of Air Particulate by Energy Dispersive X-ray Fluorescence (EDXRF). This method applies to the analysis of ambient air particulate collected on 47mm diameter Teflon Filters.

This method describes quantitative determination of elements in ambient air particulate collected on Teflon membrane filters. The elements that are determined by this method include many of the elements with atomic numbers 11 (Na) to 82 (Pb). (Note: both Na and Mg are analysed but measured as ION only).

The method assumes that the particulate is collected as a surface deposit on top of the filter media, that the particulate loading level is less than approximately 100 $\mu g/cm^2$, and that the filter matrix is relatively uncontaminated with elements over Z=9

An X-ray source removes electrons from the inner shells of atoms by exciting the atoms to energy states above the stable configuration. As electrons move to refill the ground state energy levels, the atomic system maintains its fundamental energy balance by emission of electromagnetic radiation. The emitted radiation is an x-ray whose energy is characteristic of the excited element. The samples are quantitatively analyzed by counting the number of observed x-rays over a set period, as compared with the number of fluoresced x-rays from similarly analyzed standards.

- Elements analysed by XRF : Al, Si, K, Ca, Ti, V, Fe, Co, Ni, Cu, Zn, As, Se, Zr, Mo, Pd, Cd, Ce and Pb

4.0 Apparatus

X-ray Fluorescence Spectrometer, Make- PANalytical Epsilon 5 EDXRF,

5.0 Certified Reference Material

5.1 Single-element Thin-film calibration standards from Micromatter

6.0 Procedure

6.1 Sample Preparation:

6.1.1 Open the sample chamber cover and remove the stainless steel sample trays containing the filters from the instrument.

6.1.2 Remove and invert the stainless steel sample cup holders. Then, remove them from their liners, exposing the filters. Remove the existing filters and return them to their appropriate petri dishes.

6.1.3 Remove new filter to be measured from their petri dishes and place them, facing up, onto the liners. Replace the sample cup holders over the liners and replace them re-inverted onto the sample tray.

6.1.4 Open the sample chamber cover of the spectrometer and place the sample trays back into their appropriately labeled positions.

6.1.5 Close the sample chamber cover of the spectrometer.

6.2 Preparing Spectrometer for Measurement of Filters:

6.2.1 Open the Sample Changer Measurement window by clicking on the "Open sample changer window" icon located at the top of the "PANalytical Epsilon 5 Software' window.

6.2.2 Once open, drag and drop an empty tray from the 'Tray, cup & insert' area on the labeled tray sections within the 'sample changer' area to start defining new trays for measurement.

6.2.3 Enter the sample data and other pertinent information into the 'Sample detail' area located below the 'Tray, cup & insert' area for each sample that must be measured

6.2.4 Press the start button to begin the measurement of the current samples from the measuring queue.

6.2.5 When samples in the queue measurement are finished, the results can be viewed and processed by clicking the "open window" icon followed by pressing the results button within this window.

6.3 Calibration:

6.3.1 The Micromatter thin film standard material and sample under test are analysed by XRF in the same run. The equipment is said to be in a state of acceptable valid calibration if the acceptance criteria (10% deviation) is met.

7.0 Calculations

7.1 Concentration of the elements in the sample are calculated by the software in $\mu g/cm^2$.

7.2 Results are converted to $\mu g/m^3$ by using exposed area of filter and volume of air sampled.

8.0 Reporting

a) Report the result in the desired unit e.g. $\mu g/cm^2$ up to 2 decimal places.

9.0 Records

9.1 Internal record: Calibration report of XRF, readings in Operator's logbook.

Table E-1: Standard run of Typical Elements taken on Epsilon 5, µg/cm²

Sr. No.	Element	Micromatter – XRF calibration		Deviation, %
		Specified Concentration, µg/cm²	Observed Concentration, µg/cm²	
1.	Aluminum	48.3	48.336	0%
2.	Silicon – Run 1	29.9	30.305	-1%
3.	Silicon – Run 2	29.9	29.880	0%
4.	Silicon – Run 3	29.9	29.455	1%
5.	Nickel	57.4	57.838	-1%
6.	Calcium	23.3	25.744	-10%
7.	Iron	52.4	52.633	0%
8.	Titanium	56.5	57.071	-1%
9.	Lead	57.8	58.007	0%
10.	Chlorine	32.2	32.966	-2%

Table E-2: Blank filter paper results analysed by ED-XRF (μg/cm²)

Element	Blank 1	Blank 2	Blank 3	Average
Na	-0.007	-0.007	-0.007	-0.007
Mg	-0.155	-0.152	-0.155	-0.154
Al	-0.282	-0.165	-0.282	-0.243
Si	-0.013	-0.033	0.002	-0.015
P	-1.066	-0.07	-1.073	-0.736
S	-0.027	-0.026	-0.025	-0.026
Cl	0.001	-0.003	0.002	0.000
K	0.017	-0.009	-0.009	0.000
Ca	-1.785	-1.836	-1.8	-1.807
Sc	0.007	0.006	0.009	0.007
Ti	-0.043	-0.049	-0.049	-0.047
V	-0.004	-0.004	-0.004	-0.004
Cr	0	0.001	0	0.000
Mn	-0.001	-0.001	-0.002	-0.001
Fe	0.045	-0.014	0.009	0.013
Co	-0.001	-0.001	0	-0.001
Ni	-0.029	-0.033	-0.033	-0.032
Cu	-0.027	-0.023	-0.028	-0.026
Zn	-0.048	-0.047	-0.047	-0.047
Ga	-0.009	-0.01	-0.008	-0.009
Ge	-0.003	-0.01	-0.009	-0.007
As	-0.046	-0.046	-0.041	-0.044
Se	-0.012	-0.012	-0.012	-0.012
Br	0.002	-0.004	-0.004	-0.002
Rb	0	0.002	0	0.001
Sr	-0.007	-0.002	-0.006	-0.005
Y	-0.002	-0.002	0	-0.001
Mo	-0.003	-0.005	-0.002	-0.003
Rh	-0.007	0.002	0.017	0.004
Pd	-0.011	0.003	-0.025	-0.011
Ag	-0.02	-0.014	-0.02	-0.018
Cd	-0.001	0.019	-0.019	0.000
Sn	0.01	0.006	0.003	0.006
Sb	-0.188	-0.156	-0.173	-0.172
Te	0.028	0.008	0.003	0.013
I	0.023	0.007	0.002	0.011
Cs	0.063	0.007	-0.026	0.015
Ba	0.001	0.061	0.016	0.026
La	0.044	0.075	0.037	0.052
W	-0.039	0.041	-0.031	-0.010
Au	-0.02	-0.001	-0.006	-0.009
Hg	-0.058	-0.036	-0.014	-0.036
Pb	-0.002	-0.002	0	-0.001

Table E-3 : Repeat $PM_{2.5}$ Sample runs ($\mu g/cm^2$)

Sample ID	Sample 1			Sample 2			Sample 3		
	Run 1	Run 2	Difference	Run 1	Run 2	Difference	Run 1	Run 2	Difference
Na	-0.032	-0.032	0.000	0.219	0.145	0.074	-0.069	-0.069	0.000
Mg	0.155	0.105	0.050	-0.155	-0.055	0.100	-0.155	-0.136	0.019
Al	-0.065	-0.062	0.003	-0.111	-0.082	0.029	-0.087	-0.028	0.059
Si	0.125	0.14	-0.015	0.085	0.108	-0.023	0.078	0.077	0.001
P	-1.045	-1.05	-0.005	-1.073	-1.045	0.028	-1.073	-1.073	0.000
S	0.919	0.929	-0.010	1.134	1.088	0.046	1.329	1.388	-0.059
Cl	1.007	1.001	0.006	1.371	1.315	0.056	2.48	2.428	0.052
K	1.674	1.649	0.025	1.837	1.809	0.028	1.318	1.313	0.005
Ca	-0.971	-0.983	-0.012	-1.509	-1.498	0.011	-1.595	-1.611	-0.016
Sc	0.002	-0.002	0.004	-0.002	-0.003	-0.001	0	0.005	0.005
Ti	-0.007	-0.015	-0.008	-0.029	-0.028	0.001	-0.04	-0.032	0.008
V	-0.003	0.002	0.005	0.002	0.005	-0.003	0.003	-0.002	0.005
Cr	0.005	0.005	0.000	0.007	0.007	0.000	0.007	0.004	0.003
Mn	0.089	0.095	-0.006	0.024	0.015	0.009	0.019	0.024	-0.005
Fe	1.063	1.008	0.055	0.377	0.388	-0.011	0.248	0.257	-0.009
Co	0.001	-0.001	0.002	-0.001	-0.004	-0.003	-0.001	-0.001	0.000
Ni	-0.03	-0.032	-0.002	-0.025	-0.029	-0.004	-0.029	-0.033	-0.004
Cu	-0.006	-0.009	-0.003	-0.011	-0.009	0.002	-0.009	-0.012	-0.003
Zn	0.149	0.147	0.002	0.237	0.246	-0.009	0.435	0.44	-0.005
Ga	-0.008	-0.005	0.003	-0.009	-0.011	-0.002	-0.011	-0.009	0.002
Ge	-0.006	-0.01	-0.004	-0.01	-0.009	0.001	-0.01	-0.01	0.000
As	-0.035	-0.052	-0.017	-0.06	-0.049	0.011	0.008	-0.064	0.072
Se	0	-0.01	-0.010	-0.012	-0.009	0.003	-0.012	-0.002	0.010
Br	0.023	0.026	-0.003	0.03	0.045	-0.015	0.034	0.036	-0.002
Rb	-0.001	0.008	0.009	0.008	0.005	0.003	0	0.006	0.006
Sr	0.011	0.017	-0.006	0.008	0.001	0.007	0.002	-0.004	0.006
Y	-0.001	0	0.001	-0.002	-0.002	0.000	-0.002	-0.002	0.000
Mo	0.005	-0.001	0.006	0.002	0.001	0.001	-0.007	-0.002	0.005
Rh	0.021	0.006	0.015	-0.013	0.006	0.019	-0.014	0.004	0.018
Pd	0.012	-0.001	0.013	-0.007	-0.033	-0.026	-0.011	-0.008	0.003
Ag	-0.029	-0.014	0.015	-0.025	-0.015	0.010	-0.028	-0.005	0.023
Cd	0.006	-0.004	0.010	0.015	0.016	-0.001	0.005	0.041	-0.036
Sn	0.016	0.026	-0.010	0.031	0.005	0.026	0.029	-0.011	0.040
Sb	-0.193	-0.199	-0.006	-0.0206	-0.206	-0.185	-0.148	-0.16	-0.012
Te	0.004	-0.031	0.035	-0.024	-0.001	0.023	0.003	0.01	-0.007
I	-0.007	-0.004	0.003	0.002	0.022	-0.020	0.019	0.012	0.007
Cs	0	0.031	0.031	0.023	0.002	0.021	-0.01	-0.038	-0.028
Ba	0.021	0.136	-0.115	0.068	-0.023	0.091	-0.008	0.019	0.027
La	-0.047	0.005	0.052	0.054	0.025	0.029	-0.023	-0.018	0.005
W	-0.051	-0.051	0.000	-0.051	0.025	0.076	-0.002	-0.048	-0.046
Au	-0.004	-0.012	-0.008	-0.011	-0.009	0.002	-0.015	-0.017	-0.002
Hg	-0.04	-0.031	0.009	-0.03	-0.043	-0.013	-0.047	-0.03	0.017
Pb	0.058	0.055	0.003	0.138	0.136	0.002	0.145	0.178	-0.033

Annexure-F: Non-Vehicular Source Profiles

Experimental set-up

The experimemtal set up consisted of extrcation hood connected to dilution tunnel as presented in Figure F-1 and was made of aluminium.The combustion bed for burning the biomass samples was of the size which prevents spillage of smoke outside the boundary of the face of the hood. The PM sampling point was placed at 9 duct diameters from closest point of disturbance. Probe for PM sampling was made of SS grade which conisisted of a detachable cyclone for PM_{10} and $PM_{2.5}$ sampling one at a time. The PM samples were collected on a 35 mm filter (teflon and quartz) placed in a filter holder attached to the sampling probe. A blower was used create a negative pressure inside the duct, enough high to extract all flue gas emitted and enough low to avoid quenching of combustion temperature on the combustion bed. The duct velcity was measured using pitot tube. The hood was covered from 3 sides with metal sheets to prevent spillage of smoke.

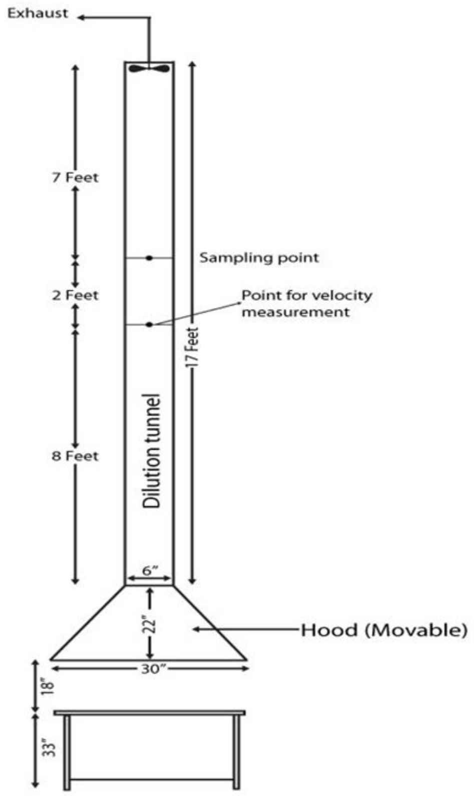


Figure F-1: Schematic diagram of the sampling set-up

Sampling

The sampling duration was kept 10 minutes for each of the biomass sample. A total of 48 samples were collected with three replicates for each PM_{10} and $PM_{2.5}$ sample collected on both on Teflon and Quartz for four types of biomass which inlcuded wheat, rice and sugarcane residues and refuse.

The PM sampling was conducted under iso-kinetic conditions.The sampling flow rate was 2.9 lpm which was calculated using the measured duct velocity which was 5 m/sec and nozzle of diameter 0.25 cm in order to maintain the iso-keinetic conditions. Particle loading for all the samples was greater than 1000 µg.

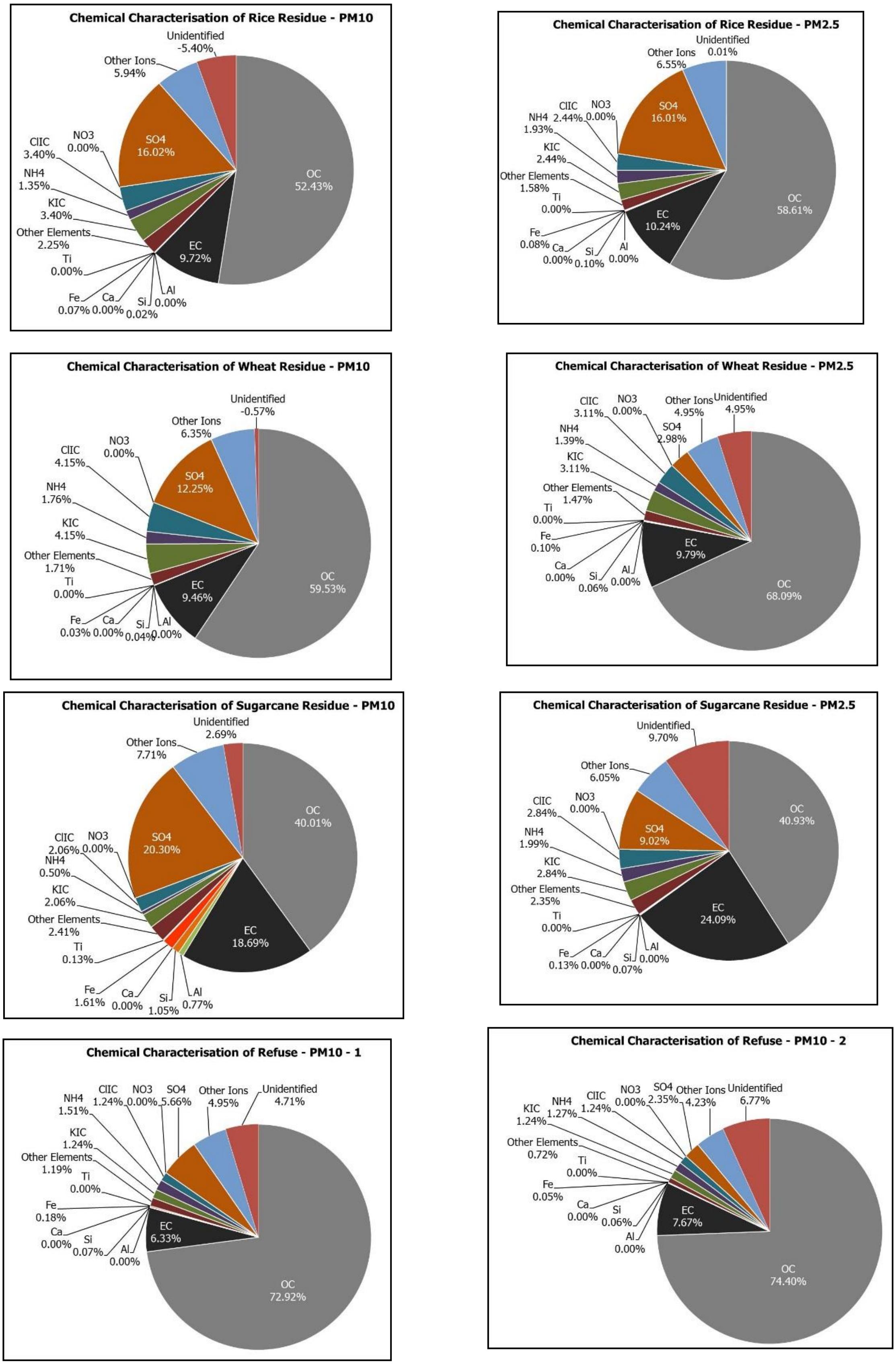


Figure F-2: Chemical characterisation of Site Specific Sources of PM_{10} & $PM_{2.5}$

Annexure-G: Source Profile

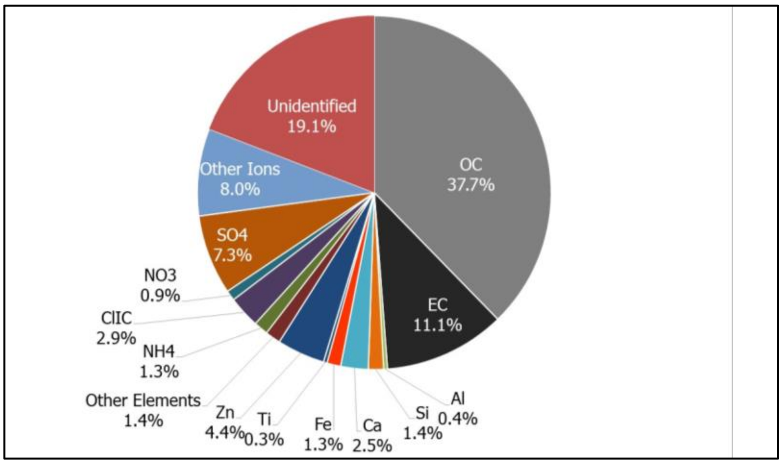


Figure G-1: Composite Gasoline

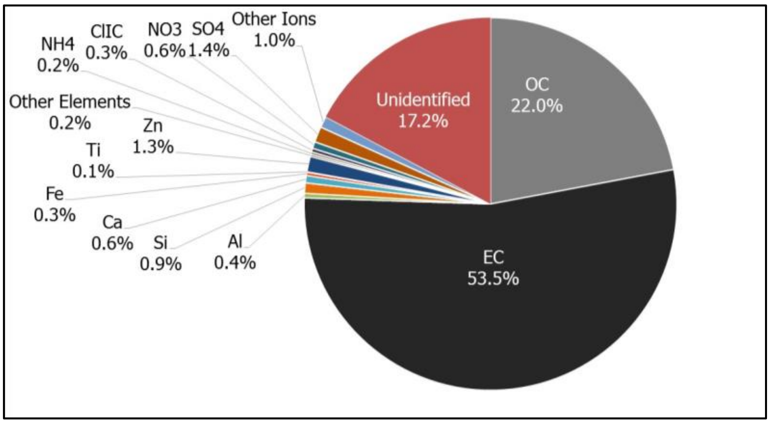


Figure G-2: Composite Diesel

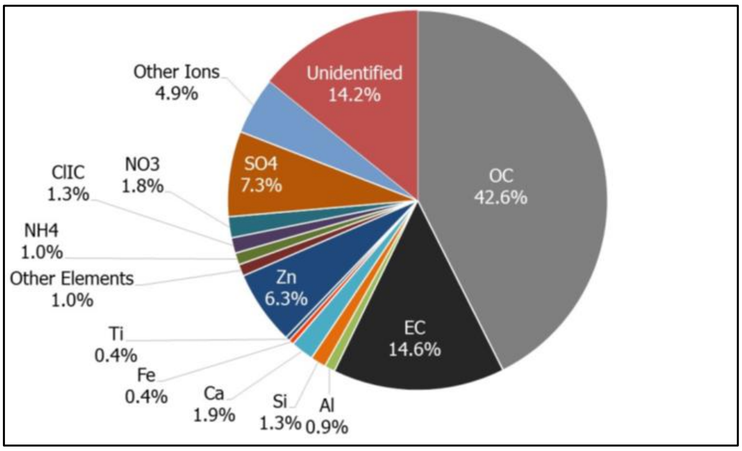


Figure G-3: Composite CNG

Annexure H– Approach to account for real-world emissions in this study

Preliminary emission estimates derived in this study when fed into the air quality model resulted in under-prediction of PM concentrations. IITK (2015) also showed significant under-prediction due to unaccounted sources and also due to background level from outside of Delhi city. The present study although showed better predictions due to accounting of background levels (through NCR emission inventory and India-scale boundary conditions), and secondary particulates (through chemistry module in-built in the CMAQ model). However, still the average ratios of modelled to observed $PM_{2.5}$ values were found to be 0.56-0.59 in Delhi and NCR, while, in case of PM_{10}, average ratios of modelled to observed values were 0.33-0.41 in Delhi and NCR. The model captured seasonal variations quite well, however the magnitude of PM concentrations were underestimated. This shows that there are still unaccounted emissions which in real world conditions are emitted from different sectors. Also, it has been observed that the model is underestimating the carbonaceous fractions more than others, and hence we estimated a possible increase in emissions of combustion-based sectors, such as transport, industrial, and biomass burning activities in real world conditions. These are the sectors for which emission inventories for India have been reported to be uncertain (Saikawa et al;. 2017, Sadavarte et al. 2016) and hence the emissions are generally under reported. Literature review has been carried out to assess the increase in emissions. Studies have shown that real-world (on-road) emissions from vehicles could be significantly higher (50%-100% ITF [2017]) than the ones measured on test-cycles in the laboratory. Similarly, due to uncertainty of reported fuel consumption and emission data limitations in enforcement, illegal use of fuels, and inefficiencies of the stack emission control equipment, industrial emissions could also be 50%-100% higher. Sharma and Dutta (2016) have shown large variations (upto 100%) in emission factors for biomass burning. Taking these variations into account, the following three emissions scenarios have been used to carry out air quality simulations:

1. Base: Assuming test cycle-based emission factors for vehicles, reported fuel consumption, and tail-pipe controls by the industries and average emission factors for biomass burning. Standard emission factors have been used for other sectors.
2. RW50%: 50% increase in emissions of transport, industries, and residential sectors.
3. RW100%: 100% increase in emissions of transport, industries, and residential sectors.

After accounting for increase in emissions in these scenarios, air quality simulations have been carried out. It was found that model performance was found to be best in the RW100% case. The average ratio of modelled to observed $PM_{2.5}$ concentrations improved from 0.56-0.59 in base case to 0.82-0.87 in RW100% scenario. For PM_{10}, this increases from 0.36-0.40 in base case to 0.48-0.57 in RW100% scenario. This performance of the model appears to be satisfactory, when compared with several previous studies. The share of different constituent species of $PM_{2.5}$ is also satisfactorily reproduced by the CMAQ model.

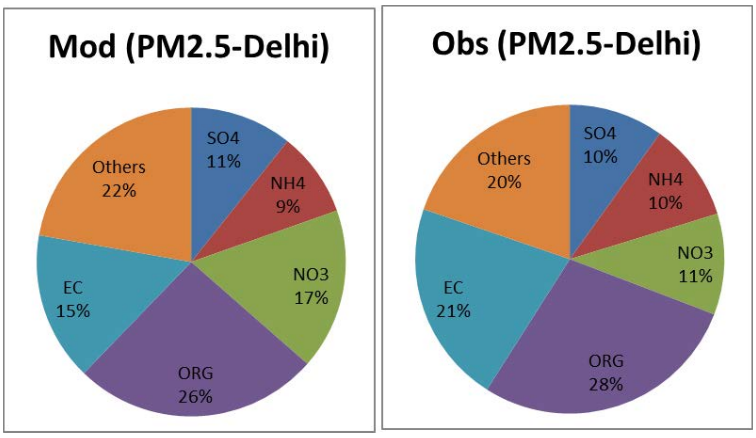


Figure H.1 Species-wise distribution of modelled and observed $PM_{2.5}$ concentrations in winter

Eventually, using RW100% emissions, the source contributions were found to be convergent with the results of receptor modelling.

Annexure- I Comparison of this study to IITK study

Source apportionment study conducted in past by IITK in 2015 attempted to quantify contribution of different sources towards PM_{10} and $PM_{2.5}$ concentrations in the city of Delhi by using receptor modelling approach. The present study and the IITK study has used a same receptor model, that is, Chemical Mass Balance Version 8.2 to preform receptor modelling exercise. However, there are differences on the dispersion modelling side. The IITK study took into account sources within the Delhi city limits only, while there are contributions from outside the city also, which are considered in the current study. Moreover, the model used in the present study takes into account the secondary particulate formation through chemical reactions between primary pollutants. The comparison of emission estimates prepared by IITK and this study is presented in Table 1.

A broad comparison of results between two studies based on Table I-1 is presented as follows:

Emission Inventory and Dispersion Modelling

1. Emissions estimated in the current study for Delhi city are 30%, 60%, and 37% higher than IITK study for PM_{10}, $PM_{2.5}$, and NOx, respectively. Initially, using the emission factors, this study also shows similar emissions as IITK report, however, after accounting for real world emissions the overall emissions are estimated to be higher in this study in comparison to the estimates of IITK. This study also included emissions of NCR which are more than 10 times of the emissions in Delhi city and have also accounted for trans-boundary contributions from rest of India and international boundaries. Consequently, in this study, the model performance has improved considerably. The average modelled $PM_{2.5}$ concentrations were about 15%-18% lower than observed values in this study. The IITK (2015) has reported low performance of dispersion model and observations were found to be 40%-180% higher than the modelled $PM_{2.5}$ concentrations. Consequently, while the IITK study did not use dispersion model for deriving source apportionment, the present study has reliably used dispersion modelling approach to derive source apportionment and generating future scenarios.
2. The present study thereafter reported a higher share of transport sector as compared to the IITK study due to accounting of high emitters and real world emissions. Road dust emissions are found to be lower in this study. Further, in this study, silt loads have been collected in both the seasons (summers and winters). Lower silt values in winter compensated for higher values in summer. On an average, somewhat reduced road dust emissions have been observed in this study in comparison to the IITK study. In others sector, landfill fire was not considered in the IITK study and this accounted for additional 5% of total $PM_{2.5}$ emissions in Delhi in the present study.
3. While the broad category of vehicles showing higher share in PM and NOx emission remained the same, the magnitude of shares are somewhat different in the two studies from transport sector. This study uses newly developed emission factors by ARAI, especially for BS-III, BS-IV vehicles, while IITK study used the estimated reduction factors for calculating emissions from these vehicles.

Table I-1. Comparison of emissions estimates done by IITK study and this study

Item	IITK	This study - Delhi	This study-NCR	Remarks
Total emissions (T/d) PM_{10} $PM_{2.5}$ NOx SO_2	143 59 312 141	185 88 428 91	2786 1447 2427 2443	Emission estimates for most of the pollutants are higher in this study as compare to IITK as the current study has accounted for real world emissions in sectors like transport, industries, and biomass burning.
Share of sources in $PM_{2.5}$ emissions				
Vehicles	20%	39%	13%	Accounting real world emissions in this study
Industries incl. PP	13%	14%	31%	Some power plants are closed / shifted to gas in Delhi since the last study
Construction	8%	8%	1%	Higher construction activities and lower silt values on roads
Road dust	38%	18%	6%	Silt samples were collected in summer and winter season. Lower silt in winters and higher values in summers were observed. Hence, on an average somewhat reduced road dust emissions were obtained.
Residential	12%	6%	25%	Higher LPG factor assumed in IITK report
Others	9%	15% (Landfill fires 5%)	24% (19% is agri burning)	In IITK study, landfill fires were not considered, which account for 5% of

Item	IITK	This study - Delhi	This study-NCR	Remarks
				total PM$_{2.5}$ emission in Delhi.
Vehicle inventory PM Vehicular shares in PM emissions	13 t/d	34 t/d	182 t/d	This study accounts for high emitters and real world emissions
Trucks	46%	32%	35%	Newly developed emission factors by ARAI have been used in this study, especially for BS-III, BS-IV vehicles, while IITK study used estimated reduction factors for these vehicles.
2-w	33%	26%	14%	
3-w	2%	18%	15%	
Cars	10%	12%	11%	
Bus	5%	4%	12%	
Others	4%	8%	13%	
Vehicle inventory NOx Vehicular shares in NOx emissions	113 t/d	348 t/d	1449 t/d	This study accounts for high emitters and real world emissions
Trucks	21%	22%	32%	Newly developed emission factors by ARAI have been used in this study, especially for BS-III, BS-IV vehicles, while IITK study used estimated reduction factors for these vehicles.
2-w	9%	23%	15%	
3-w	6%	16%	8%	
Cars	17%	12%	9%	
Bus	27%	20%	16%	
Others	20%	7%	20%	

Further, the comparisons of sectorial contributions obtained from receptor modelling using CMB8.2 in both the studies are discussed in subsequent sections.

Receptor modelling

PM$_{2.5}$

Overall, the results of this study are more or less consistent with the IITK report, with slight variations in magnitude (Figure I.1). In winter season, contribution of dust in PM2.5 concentrations is found to be somewhat higher in this study, and the share of biomass is lower. Higher penetration of LPG in the last 2-3 years could be the most plausible reason for reduction in biomass contributions. Moreover, this study does not include October, when agricultural burning is found to be prominent. During summer season, the share of vehicles in this study is somewhat higher in PM$_{2.5}$ concentrations and the share of industry is lower. This is possible because sites of monitoring considered in the two studies were different. Also, the average wind speed during winter season was similar, that is, 1 m/s in both the studies while in summer, during IIT Kanpur's study, average wind speed was 3 m/s and during this study it was 1.6 m/s leading to less favourable dispersion conditions. This could lead to higher contributions in this study from local sources like vehicles in Delhi.

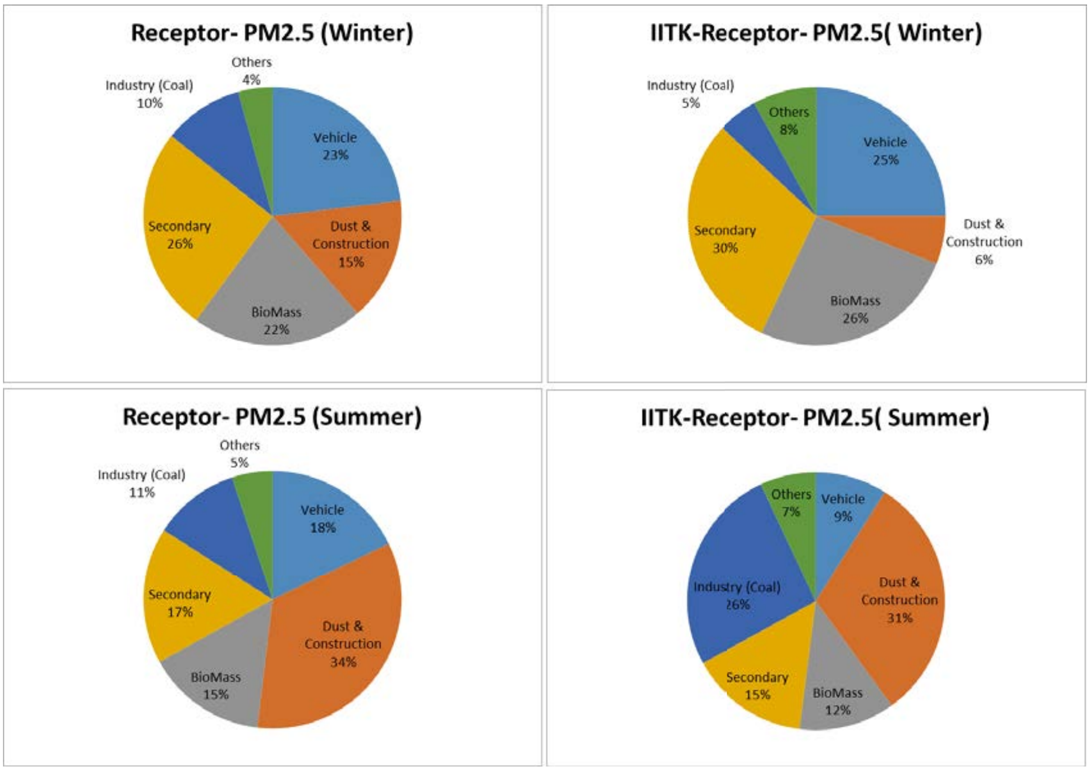


Fig.I.1: Sectoral contributions from receptor modelling in winters and summers: this study and IITK (2015)

PM$_{10}$

Results of source apportionment of PM$_{10}$ show that dust is a major contributor to PM$_{10}$ concentrations (Fig. I.2). The share of dust is 31% in winter, which increases to 42% in summer. In comparison to the IITK study, this study shows lower contribution from industrial coal use, which can be attributed to closure and limited operation of some of the power plants in the vicinity. Contribution of the transport sector in PM$_{10}$ is somewhat higher in this study (15%-18%) than the IITK (2015) study (6%-20%). This is possible because sites of monitoring considered in the two studies were different. Moreover, the wind speeds during summer were lower in the present study leading to lesser dispersive conditions and hence higher contributions from local sources like vehicles in Delhi.

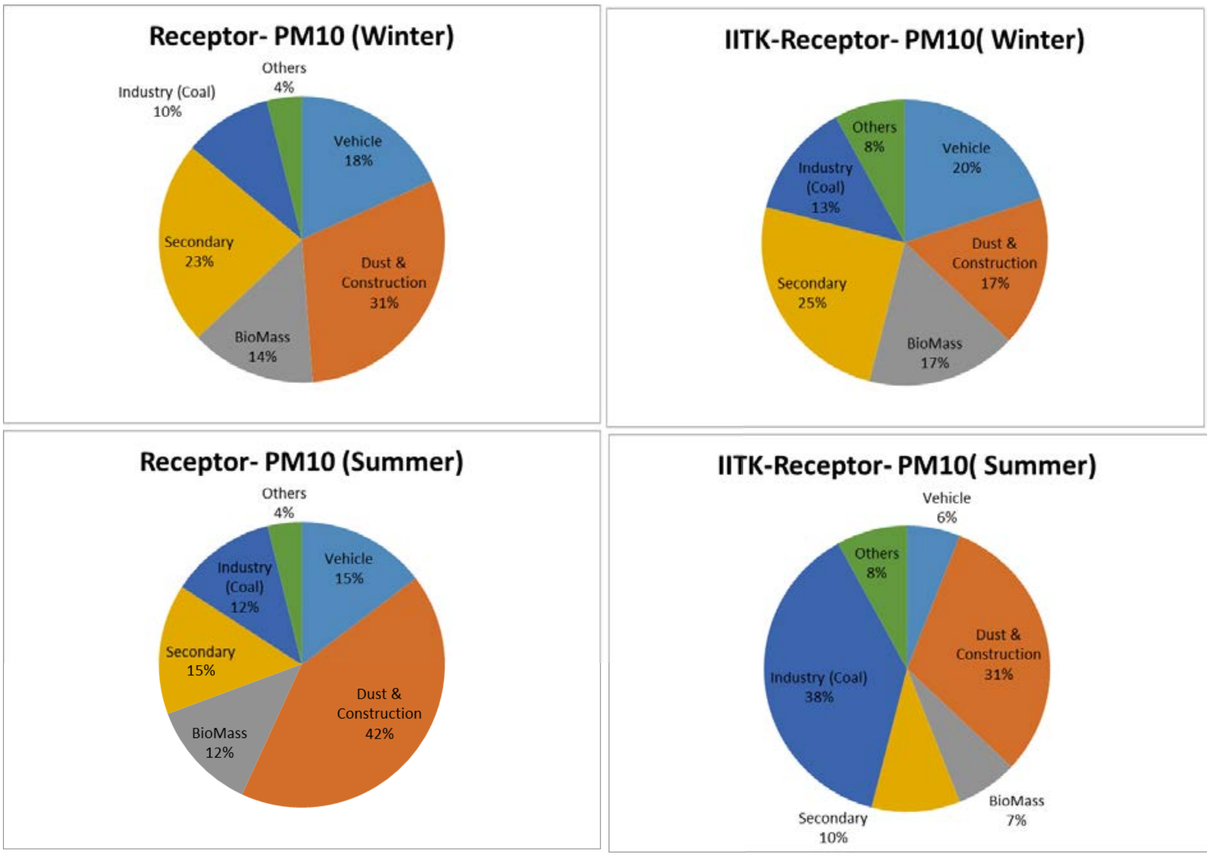


Fig. I.2: PM$_{10}$ Sectoral contributions from receptor modelling in winters and summers: this study and IITK (2015)