

Exam in Methods for Environmental Monitoring, FKFN35

Saturday June 1 2019, 8:00-13:00, IKDC, room 567

Use a separate sheet of paper for each question. Note the number of papers handed in on the cover and mark which questions you have tried to answer.

Answer the questions in English or Swedish.

You may very well use figures/drawings or tables/lists in your answers.

Back pack, telephone and books, etc. at the coat hangers, and not by your desk.

To pass, minimum 50 % on the written exam.

Total points: 56p (50 % = 28p).

1. Biomarkers (6p)

Below are a substance with health risks. From the given data motivate what's most suitable for monitoring occupational exposure; external or internal measurement, sampling matrix, sampling time, and if biological monitoring exposure is deemed necessary what type (internal does, effective dose, specific or unspecific method).

- Specific
 - Analytic specificity
 - Metabolic specificity
 - Source specificity
- Informative
- Validated
- Known kinetics
 - Half-lives
- Better than the alternatives (external measurement)
 - Air sampling
 - Surface & dermal monitoring

a) Metallic (inorganic) mercury is absorbed by inhalation while other absorption is low. It is distributed evenly in the tissues. The organic compounds are lipophilic and are readily absorbed by biological membranes. Exposure to organic mercury compounds is now unusual in industry. Metallic mercury has a half-life in blood of 1 week, in urine 1-2 months and in the brain a couple of years. Organic mercury, common in fatty fish, has a half-life in about 1,5-2 months in blood and slightly longer in faeces. The preferred analytical method ICP-MS is a convenient way of analyse mercury but the method can't distinguish between metallic and organic mercury. (4 p)

b) What is ICP-MS? Describe what is achieved in each step in one or two sentences. (2p)

Answer:

- a) *Urine, morning before work-day to get highest concentration creatinine. (slide 42; > 100 h, sampling is not critical). Since metallic and organic mercury in blood can't be discern it is not source specific but it is metabolically specific. It measures internal dose with a specific method.*
- b) *3 major steps:*
 - i. *Vacuum inlet to admit the samples to be studied to the ion source*

- a. *Ion Source: For producing gaseous ions from the substance being studied.*
- b. *Separator (Analyzer): For resolving the ions into their characteristics mass components according to their mass-to-charge ratio.*
 - ii. *Eventually, fragment the selected ions and analyze the fragments in a second analyzer*
- c. *Detector System: For detecting the ions and recording the relative abundance of each of the resolved ionic species.*
 - iii. *Process the signals from the detector that are transmitted to the computer and control the instrument using feedback.*

2. Optical techniques (10p)

2A (3p) **Discuss** advantages and disadvantages of satellite imaging versus laser radar (lidar) in terms of: active or passive technique, coverage and resolution in time and space. Give **two examples** of how to retrieve range information with lidar.

2B (2p) Explain with your own words **how** spectroscopic features, such as absorption and fluorescence, differs between samples in solid and gaseous phase and **why** this is so.

2C (1p) The Sun's surface temperature is 5791 K and has a peak emission at 500 nm wavelength. Indicate the approximate **peak emission wavelength** of the Earth at room temperature give the **name** of the region in the electromagnetic spectrum.

2D (4p) Light impinges on an air volume from the left, see figure below. The volume has the optical properties of absorption coefficient (μ_a) and scattering (μ_s) both in the units of km^{-1} . For the cases of high and low optical properties, fill in the resulting reflected- and transmitted **light intensities** in the table with values from 1 to 3 (arbitrary unit).

	Low μ_a	High μ_a		Low μ_a	High μ_a
Low μ_s					
High μ_s					

3. Dispersion and source/receptor modelling (10p)

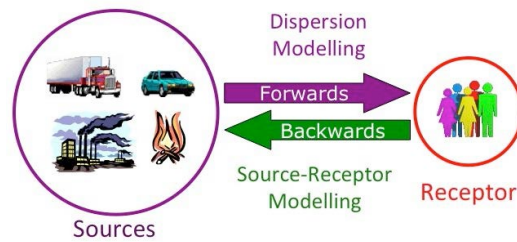


Figure 1. Only included as illustration.

- (a) Describe which two types of input data area absolutely crucial for dispersion models and how they are used in the model with a few sentences (Hint: not measurements). (2p)
- (b) Mention with a few sentences how you can calculate the air pollution concentrations with a dispersion model. (2p)
- (c) Explain the principles of source/receptor models. Explain it by including a description of the data matrix, source profiles, and source contributions. No equations and explanation of difference between chemical mass balance and factor analytical models needed. (3p)
- (d) Figure 2 shows an example of a PMF source/receptor model run for Quillota in Chile, where they have highlighted how two smelter factories (“Smelter 1”, and “Smelter 2”), soil dust, traffic, and a sea spray source contribute to the concentration of PM10 during different months. How is the PMF model able to distinguish how much Smelter 1 and Smelter 2 contribute to PM10 mass concentrations? Use the information from the source profile in Table 1 to reason around your answer in a few sentences. (3p)

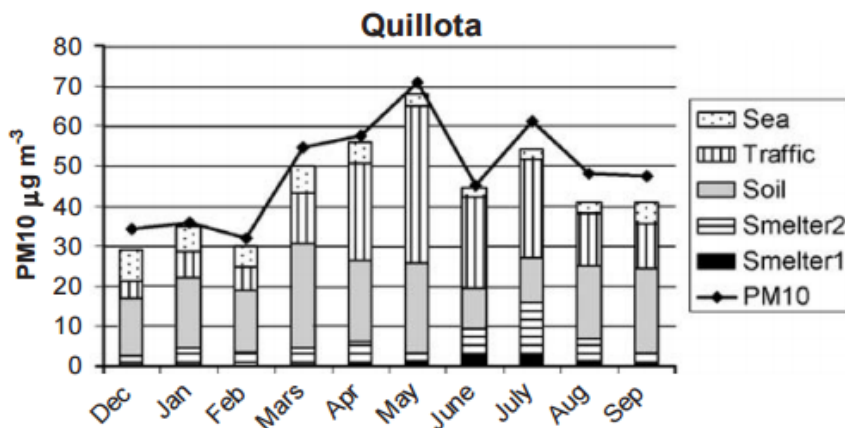


Figure 2. PMF source/receptor model results of apportioned PM10 mass concentrations in Quillota, Chile for different months during Dec 1999 – Sep 2000. PM10 denotes the measured PM10 aerosol mass concentration, and the sources contributing to the PM10 mass concentrations are Sea spray, Traffic, Soil dust, and two smelter factories (Smelter 1, and Smelter 2). From Hedberg et al., 2005.

Table 1. The source profiles obtained by PMF source/receptor modelling of PM10 particle metal concentrations in Quillota, Chile.

Source profile concentrations obtained from PMF (average contribution ng m^{-3})

Conc. (ng m^{-3})	Smelter 1	Smelter 2	Soil	Traffic	Sea
<i>(a) For Quillota</i>					
Ag	0.0	0.3	0.0	0.0	0.0
Al	0.2	24.3	1293	20.6	64.2
As	15.7	12.9	0.0	2.5	0.5
Ba	0.2	0.6	10.1	5.1	0.0
Bi	1.1	0.0	0.0	0.0	0.0
Br	0.0	0.0	0.0	20.0	11.6
Ca	30.7	0.0	645	139	35.5
Co	0.1	0.0	0.4	0.0	0.1
Cr	0.5	0.1	2.0	1.5	2.3
Cu	34.7	25.3	5.4	0.0	4.0
Fe	21.3	26.4	961	36.4	31.0
K	14.1	15.5	314	203	94.8
Mg	0.5	1.6	222	7.2	166
Mn	0.2	0.5	28.5	1.3	0.0
Mo	0.4	0.7	0.1	0.2	0.0
Na	0.1	0.1	118	0.2	1439
Ni	0.1	0.0	0.0	0.8	1.4
Pb	0.3	22.2	6.7	30.9	0.0
Rb	0.1	0.1	1.5	0.3	0.0
S	230	808	159	648	1058
Sb	0.1	0.6	0.1	0.4	0.0
Si	7.2	0.5	3802	254	305
Sr	0.1	0.1	4.3	0.6	1.0
Ti	0.0	1.3	85.3	0.0	3.8
V	0.1	0.5	2.3	1.0	0.7
Zn	0.0	27.9	8.1	11.3	4.8
Sum	358	969	7667	1384	3224

Answers:

a) Emission data (emission database, how much each source emits), and meteorological data (how are the winds and other meteorological factors spreading out the pollutants)

b) The emission at one point taken from the emission database is spread out like a chimney plume to the surroundings using the information from meteorology. The model is discrete, meaning pollution from one time and one box is transported in a small time phrame to the other surrounding boxes.

c) S/R modelling relies on the principle that measured concentrations (one part of the data matrix) during one time instance can always be represented as the product of the source profile and the source contribution with all sources added together. A source profile is

basically the relative emissions of different compounds from a specific source, which are used in the S/R model. The source contribution is the relative (or with more advanced models, the absolute) contribution to the measured concentration of a compound from the different sources, which influence the compound. Source contribution can be retrieved from each time instance. For each time instance, the model is looking at how relative concentrations of measured compounds “look like” compared to source profiles, and decides how each source profile adds up to the total measured concentration, which is the source contribution. This doesn't give extra points: “Some models take into consideration larger uncertainties in measured compound concentrations, and put less effort into matching this specific compound, and puts more weight into identifying the correct sources for the other compounds.”

d) There can be many answers to this question. One example: Smelter 2 emits relatively high concentrations of Al compared to other elements, which distinguishes it from Smelter 1. So, high concentration of Al together with several other elements indicates Smelter 2 dominated contribution, and if PM10 concentration is relatively high at the same time, it means smelter 2 contributes significant amount of particle mass concentrations to PM10. For smelter 1, we have rather high concentrations of Ca, which can distinguish it from smelter 2. If we measure significant concentrations of both Ca and Al at the same time for the same sample, it means that both smelters contribute to Ca and Al and maybe to PM10 (if PM10 mass concentration is relatively high).

Even if the element contribution to total particle mass concentration is low in the specific source, it can still contribute a with a high mass concentration to PM10, since the source tracers are telling if the source contributes in general to particle mass, and not only to the source tracers. For example, if a specific source tracer concentration is high (but still very low in comparison to total PM10 mass concentration) and the total PM10 mass concentration is high at the same time, the source/receptor model will know that this specific source contributes to high mass concentrations of PM10. Even if the source tracer concentration is very low compared to the total PM10 mass concentration.

4. Nuclear microprobe analysis (12p)

^{14}C analysis

A significant part of the atmospheric aerosol mass contains carbon. The figure below shows the results of a one-year source apportionment study (April 2008-April 2009) performed at the background station Vavihill in southern Sweden. Two of the analytical techniques used in the source apportionment study are ^{14}C analysis and levoglucosan analysis.

(a) ^{14}C is produced naturally as well as by anthropogenic activities. Mention two human activities known produce artificial ^{14}C . (1p)

(b) What information will the ^{14}C analysis of aerosols give regarding the aerosol sources, and why? (1p)

(c) ^{14}C in aerosol samples can be measured by the technique accelerator mass spectrometry (AMS). Describe the basic principle of this measurement technique. (3p)

(d) What is levoglucosan a tracer of? (1p)

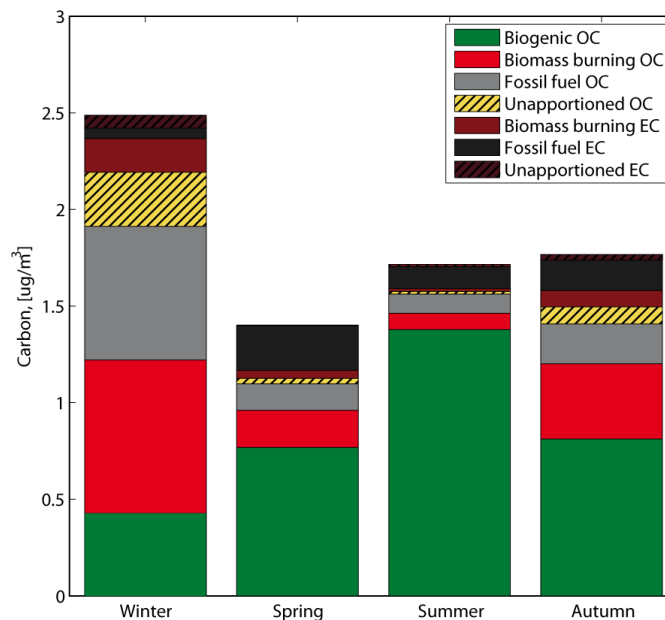


Figure 3. From: Genberg et al, *Atmos. Chem. Phys.*, 11, 11387-11400 (2011).

PIXE

e) What area of the periodic table is PIXE good at analysing, why? (1p)

f) What are the limits of PIXE analysis in terms of sample thickness? (1p)

g) What result will be obtained by using PIXE in conjunction with a nuclear microprobe? (1p)

h) There are several other methods based on the detection of characteristic X-rays. Mention two of them and discuss one in more detail comparing with PIXE. (3p)

Answers:

- a) Nuclear weapons, nuclear reactors, accelerator laboratories (two should be stated for 1 p)

- b) ^{14}C distinguishes between fossil sources (free from ^{14}C) and modern sources (natural and bomb ^{14}C e.g. in biomass burning and natural aerosols) (1 p)
- c) Accelerator mass spectrometry (AMS): Carbon (size: mg) in sample is extracted to graphite which is pressed into a sample holder and placed in an ion source. Negative carbon ions are extracted in a Cs sputtering source ($^{12}\text{C}^-$, $^{13}\text{C}^-$, $^{14}\text{C}^-$). Apart from $^{14}\text{C}^-$, also molecules are extracted with almost equal mass as $^{14}\text{C}^-$, eg. $^{13}\text{CH}^-$: these need to be removed prior to detection. The basic steps are: ion production in ion source, energy analysis in an electrostatic analyser, mass selection in a low-energy dipole magnet, acceleration to 240 keV, stripping (which breaks up molecules and shift the ion beam from negative to positive: this required high energy of the ions), mass, energy and charge selection in magnetic field, final analysis in electrostatic analyser. The system switches between the different carbon isotopes to get the percentage ^{14}C in the sample. The measurement is done relative to standard of known activity and ^{14}C -tree blanks. (3p)
- d) Biomass burning (1 p)
 - e) Elements with proton number greater than 11 (elements above Na), the energies of characteristic X-rays increase with proton number and are easier to detect.
 - f) Only the surface can be analysed, no depth profiling is available.
 - g) A quantitative elemental map/image of the sample surface, over the scanned area.
 - h) XRF - compact lab instrument, but lower sensitivity, similar range of resolution; SR-XRF - higher sensitivity, but requires a dedicated research facility (e.g. MAX IV), similar range of resolution, EIXE - very compact but poor sensitivity, higher resolution.

5. Sampling strategy (6p)

(a) In which environment should one measure air pollution in order to quantify a typical average exposure for humans living and working in a town? Please describe an example of such an environment (2p)

(b) Assume that Malmö town has decided to ban diesel cars in downtown Malmö by January 1, 2030. What is your measurement strategy to measure the impact of the new legislation on air quality? Describe where in town you would like to measure the air pollution, the time period of measurements, and which gaseous and particulate compound you would like to measure. You know that the number of diesel cars will go down due to the new regulation. But, beside counting the number of diesel vehicles, what other non-pollutant measurements would you like to perform to control that the air pollution situation has improved? (4p)

Answers:

(a) Urban background. Typically roof level measurements on high building. In a green area in the town centre, at least 100 meters away from busy roads is also okay.

(b) I would measure NO_x and BC, which are emitted in large amounts by diesel vehicles. Would measure at a highly trafficked street. I would measure a full month at least before the new regulation, and a full month after regulation, so December 1 2029 – January 31 2030. Could be longer as well to get seasonal variations. But, for example one day would not be enough, if for example this day is with winds that are not typical for this current day, than it might be that December appears cleaner than January. As non-pollutants, I would measure wind direction and speed to make sure that we do not have these kind of atypical concentration and wind effects. Or, if you think that CO₂ is not an air pollutant (which it is not, just a greenhouse gas), I might measure that as well. You can relate pollutant concentrations to CO₂ concentrations and achieve an emission factor per kg fuel burned. In this way, you can measure if you have lower emissions than previously. Emission factors are really out of scope of this course, but if you answer this, it is also ok.

6. Aerosol measurement techniques (12p)

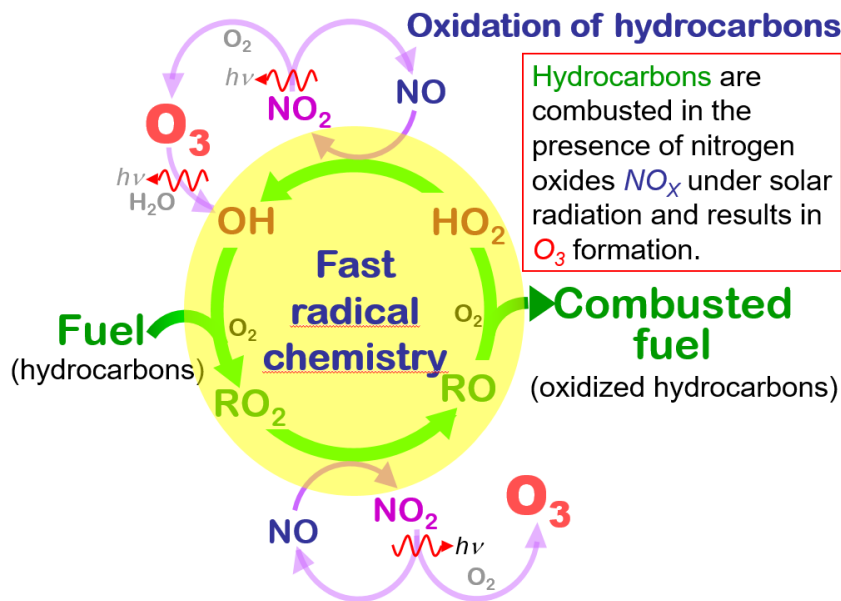
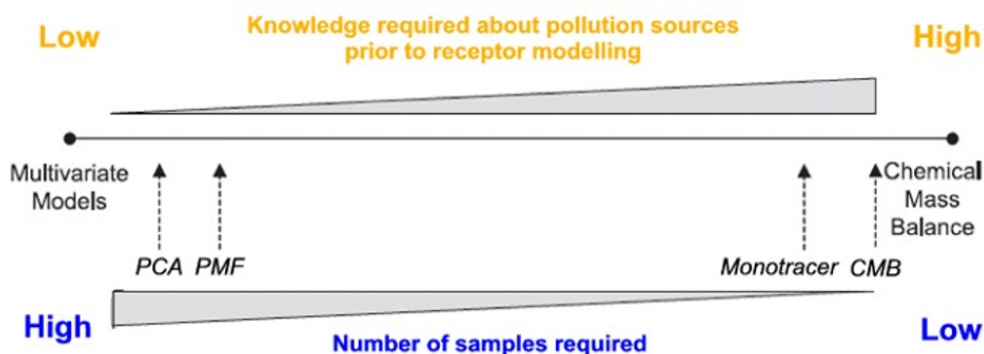


Figure X. Ozone formation.

- State two reasons why ground level ozone is considered a pollutant. (1p)
- Describe the basic principle of a technique used to measure ground level ozone concentration briefly (2p). Comment on whether the technique you describe is a reference method or not (1p).
- Ozone concentration measurements are the responsibility of the Swedish Environmental Agency (Naturvårdsverket). NO_x and many other air pollutants are monitored by the municipalities (kommunerna). How come there is this difference? (2p)
- Are ozone measurements useful for source receptor modelling? Motivate your answer! (1p)



Trade-off models between

- Information on the emission source profiles of the relevant sources
- Number of samples that can be sampled and analyzed (and available tracers)

Figure X+1. Comparison of source-receptor models.

e) Carbonaceous (carbon containing) material is a large fraction of PM_{2.5}. It can be difficult to know the best way to deal with high concentrations because many sources and processes contribute. Often mass spectrometry is used to characterize the composition, in order to enable source apportionment. This can be done through offline filter samples, which gives molecular information but poor time resolution, or online aerosol mass spectrometry (AMS). For AMS the time resolution is very high as the composition is essentially measured in real time, e.g. updated every minute. However, there is little molecular information as the molecules fragment into smaller pieces in the measurement.

Which approach (offline or AMS) is preferable for multivariate models? Chemical mass balance models? Motivate your answers! (3p)

f) State one advantage each of multivariate and chemical mass balance models respectively which is not shown in Figure X+1. (2p)

Answers:

a) *It is harmful to human health and damages vegetation e.g. crops. Also it is involved in secondary particulate matter formation through oxidation of gas phase species. [these are three reasons]*

b) *UV-photometric method, which is the reference method for ozone. Air is sampled through a filter which removes particles that would otherwise interfere with the measurement. The air is irradiated with UV-light, which is absorbed by the ozone in an absorption cell. The UV-light is measured, and the reduction in intensity is proportional to the ozone concentration. Ozone is periodically removed by use of a catalytic converter in order to get the intensity with no ozone in the cell, for reference.*

c) *This is because ozone is a secondary pollutant, which is not emitted directly from any activity that the municipalities can control through e.g. restricting traffic, which can be used to combat NO_x. The ozone levels depend on NO_x, hydrocarbon and sunlight abundance. Ozone formation takes time, which means the levels are elevated some distance downwind of the emissions. Therefore, it is better managed by SEPA, which works on a more overarching level.*

d) *No, because they do not give direct information about emissions from a source, see c) above. [Yes, if one defines the processes of secondary pollutant formation as sources, which is however not typically the case].*

e) *For multivariate models AMS is preferable because the number of samples is very high, as each mass spectrum is a "sample". For chemical mass balance offline mass spectrometry is preferable because when predetermined source profiles are used, there is the difficulty of translating the profiles into the fragments measured by AMS.*

f) *Multivariate: one can find "surprise" sources which were not known beforehand. Chemical mass balance: interpreting the results, e.g. the contribution of a source such as traffic exhaust is trivial, because one specifies beforehand exactly how traffic is defined in the model.*