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University by definition rather than in reality

105 employees

~ 500 academic students

Research interests:

(Inorganic) analytical chemistry

Sample pretreatment

Atomic spectrometry

Flow-injection analysis

Molecular flame emission

Multivariate mathematical modeling

Main projects on air pollution

Tracking sources of airborne dust through PLS modeling of ICP-OES, ICP-MS and VIS-NIRS data

Detection of gaseous sulphur species measuring molecular emission from "cold" flames

Overview of dust modeling

Problem: Where is the dust coming from

Solution:

- Samples from suspected dust sources collected in same manner as real samples
- Dust on filters scanned for reflectance VIS / NIR
- Dust realeased from samples through microwave digestion
- Element composition of digests determined with ICP-OEC /ICP-MS
- All experimental factors (element conc. and reflectance values) used for modeling individual sources using a PLS algorithm
- Model tested by adding up individual contributions
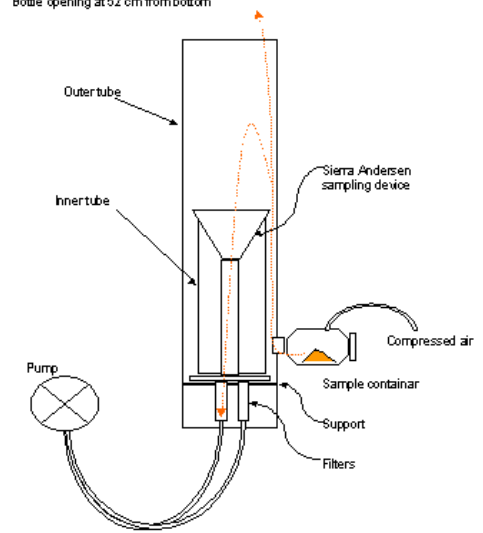
Sample	Soil	Asphalt	Exhaust	Salt	Total %
3054F	0,09	0,36	0,30	0,24	99
3069F		0,43	0,42	0,15	100
3392F		0,12	0,76	0,07	95
3294F	0,11	0,42	0,44	0,08	105
3371F			0,91		94
3388F	0,23	0,70			93
3578F		0,62	0,35	0,07	104
3580F	0,07	0,45	0,33	0,07	92
3581F	0,30	0,42	0,22		94
3594F	0,41		0,36	0,16	95
3593F	0,06	0,21	0,41	0,22	90
3602F	0,36	0,43	0,06	0,09	94
3603F	0,07	0,41	0,37	0,09	94
3604F		0,50	0,40	0,12	102
AVG(%)	**0.12**	**0.37**	**0.38**	**0.11**	**97**

Lecture overview

- Background - airborne pollution in Reykjavík

- The analytical problem

- ICP-OES and ICP-MS data

- NIR Spectroscopy

- Shielding factors and iterative modelling

- Model results

- Concluding remarks

Project funded by Nordtest

Nordtest Technical Report 544

Method for determining the composition of airborne particle pollution

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Arngrímur Thorlacius, IceTec

Steinar Larssen, NILU

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Air pollution in Reykjavík

Until rather recently the inhabitants of Reykjavík considered their home town to be exceptionally clean and free from pollution. This is however definitely not true anymore, as the EU limit values for ambient particle pollution are now exceeded on several occasions each winter.
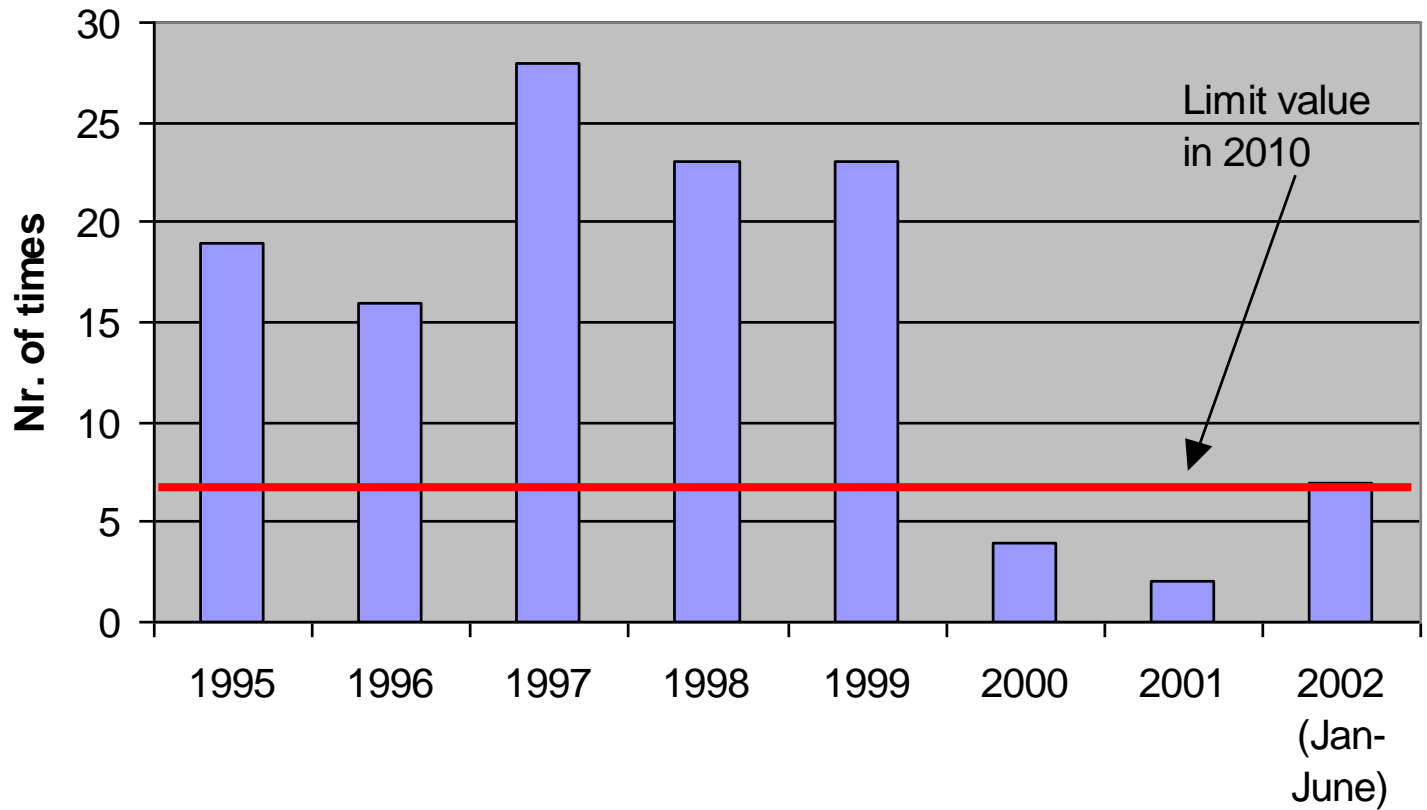
After years of debate on the causes of this problem the results from the model work described in this lecture, are generally thought to give a satisfactory explanation.

Seasonal variation of airborn dust
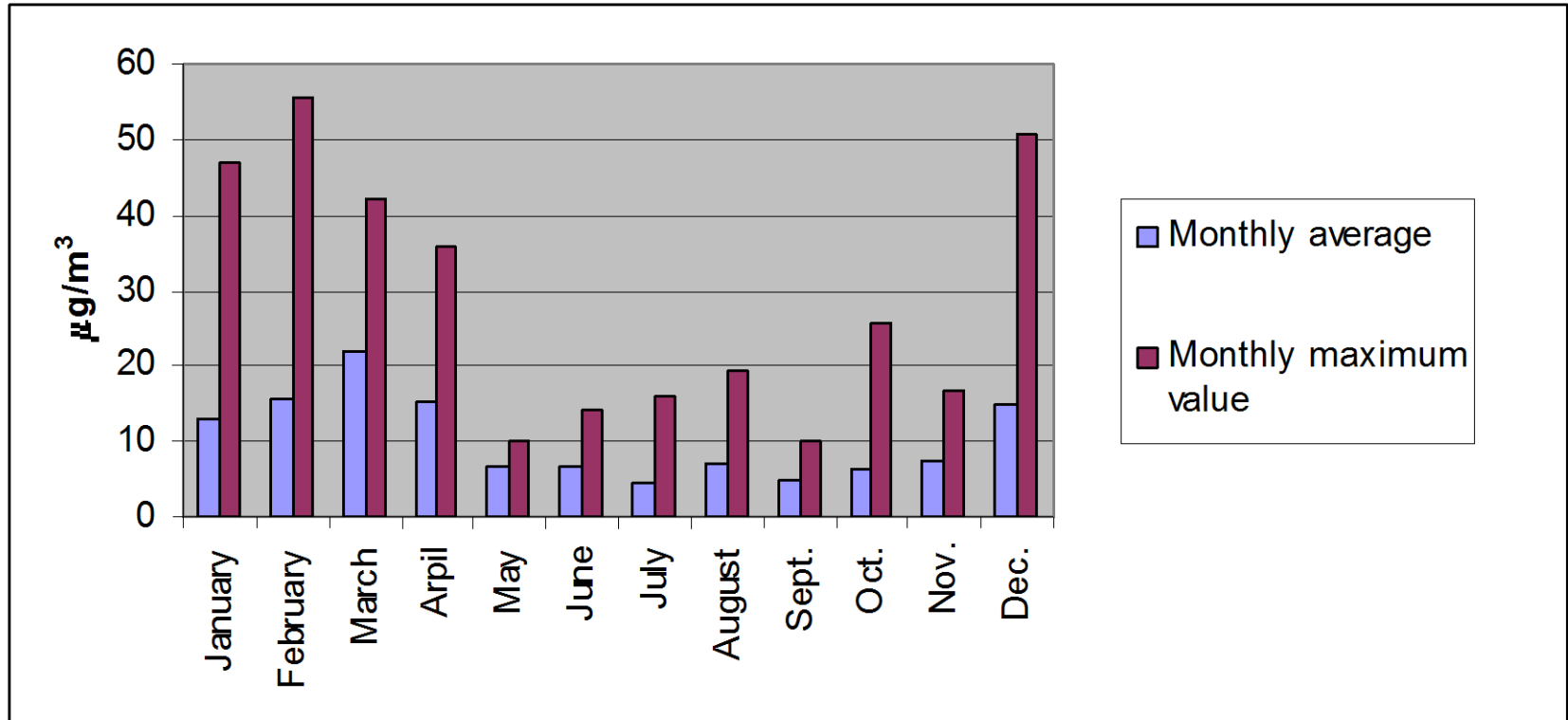
Monthly averages and maximum 24 hour value for PM10 at Miklatorg in 2001

Number of times exceeding 50 µg/m3

The analytical problem

- Sources of airborne particulate pollution undergo a series of decomposition and separation processes before yielding the minute particles that constitute the airborne dust. Sampling a relevant fraction from a source is therefore difficult.

- The sources have considerable overlap in elemental content i.e. it has been impossible to link a certain source to a definitive element or analyte, hence a multivariate technique is needed.

- In particular, the similarities between the elemental compostion of asphalt and soil were expected to cause problems for a successful tracking of sources, especially as these two sources were expected (and found) to be of major importance.

The solution tested

Samples of suspected pollution sources were powdered (if needed) and then flushed by a stream of compressed air through a channel, passing a dust sampler of the same type as used for collecting real dust samples.

Thus samples of source materials could be collected in a manner comparable to the collection of real dust samples.

The solution tested - cont.

All samples, from sources and real
airborne pollutionion, were analysed for
all elements that were expected/suspected
to be present in sufficient quantities.

The solution tested - cont.

Near infrared (NIR) and visible region scans from the surface of all filters were collected before the destructive elemental analysis. This was done in hope of getting information on the organic content, which was expected to be quite different in soils as compared with asphalt and soot.

Tested sources

- Soil (two samples collected in the ouskirts of Reykjavík)
- Asphalt (simulation of wear by studded tires on asphalt cores from a main road in vicinity of air dust sampler)
- soot (collected directly from exhaust pipes of a diesel and petrol car, respectively)
- Brake lining (from the ventilation system of a brake repair shop)
- Salt (seaspray and salting of streets)

Particle Sampling Device
Outer tube   200 x 31 cm
Inner tube   83 x 20
Support at 15 cm from bottom
Bottle opening at 52 cm from bottom

Modified dust sampler

Outer tube

Inner tube

Sierra Andersen sampling device

Compressed air

Pump

Sample container

Support
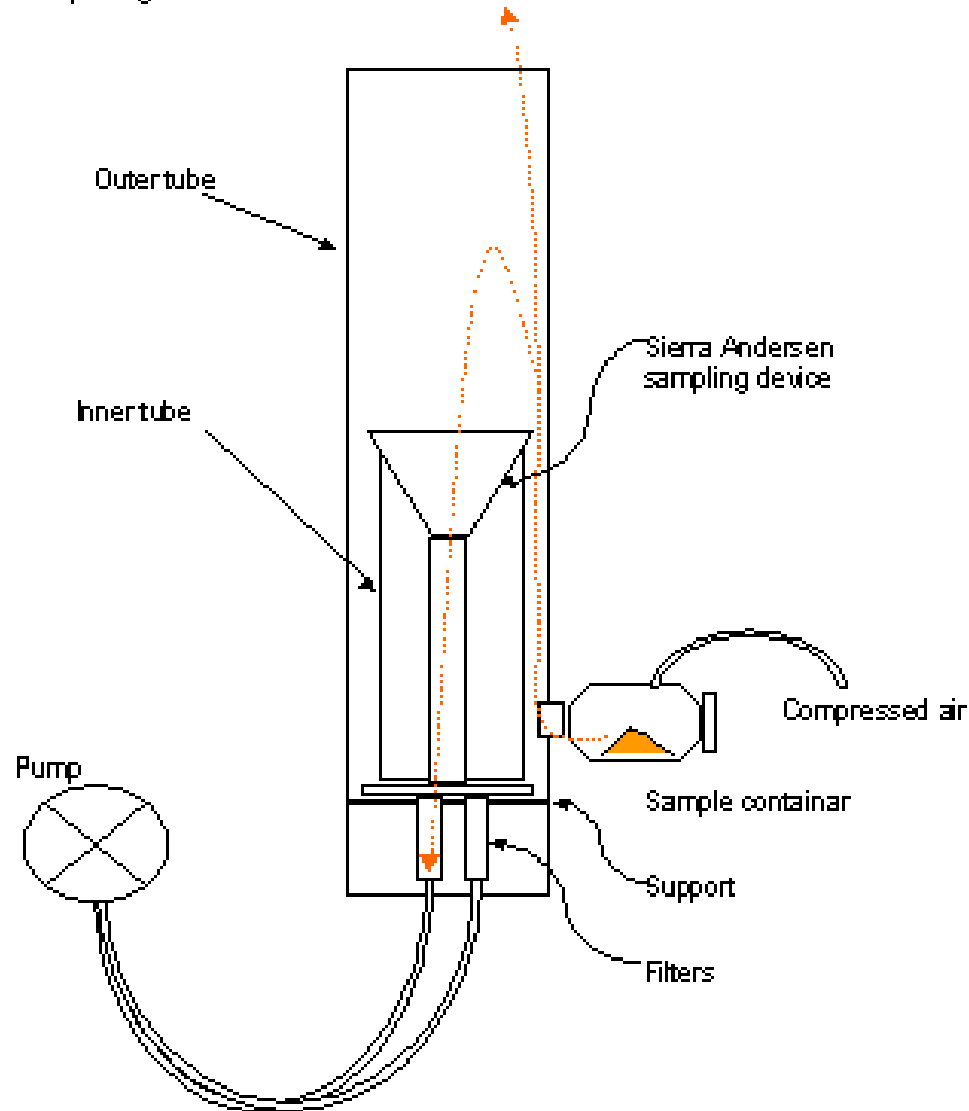
Filters

Sampling car exhaust (soot)

Sampling setup for soil, asphalt and brake lining

Creation of asphalt dust thorugh simulation of wear by studded tires

Decomposition of filter samples

Dust samples were decomposed in teflon bombs by microwave heating in 3mL of nitric acid and 2mL of hydrogen peroxide (bombs by Parr (USA) and heating in a household oven (Electrolux, Sweden)

Heating program

	time (min)	Effect (W)
Step 1	1	450
Step 2	5	150
Step 3	2	450

Digested samples filtered (0,45μm) and diluted to 12 mL. This was used without dilution for the ICP-OES determinations, but an aliquot was diluted six times for the ICP-MS measurements.

Note: Crystalline silicates undissolved

ICP-OES

(Inductively Coupled Plasma Optical Emission Spectrometry)

	wavel. (nm)
Ca	422.673
Mg	285.213
K*	766.491
Na	589.592
Fe	259.940
Mn*	257.610
Zn	213.856
Cu	327.396
Al	396.152
B*	249.773
P	213.618
S*	182.040
Si * *	288.158

Instrument: Spectroflame D, Spectro Germany.
Plasma: Ar, 1100W, vertical mount
Integration time: 3 x 3 sec. + 3 x 3sec. backgr.
Nebuliser: Cross flow, double-pass spray chamber

• Results omitted due to the large portion of results that were below the estimated detection limits

** Results omitted since digestion blanks yielded high and uneven mesurements

ICP-MS analysis

(Inductively Coupled Plasma Mass Spectrometry)

Analytical isotopes

As-75 *

Ba-138

Cd-114 *

Co-59

Cr-53 *

Cu-65

Hg-202 *

Nb-93

Ni-62 *

Pb-208

Sr-88

Ti-49

V-51

Zn-66

Zr-90

Instrument: Renaissance TOFMS, Leco USA.
Effect: 1200W
Ar flow rates: 15,5 L/min. (total)
 0,98 L/min. (nebuliser),
 1,15 L/min. (aux.)
On-line dilution: ca. 26 times with 0.1% HAc

- Results omitted due to the large portion of results that were below or only marginally above the estimated detection limits

Pretreatment of elmement concentrations

- To get comparable data all results have to be corrected for the amount dust collected, to give % or ppm of analyte per mass of dust.

- Results close to the LOD are set to zero to avoid blowing up of noise for the smallest/lightest dust samples.

- When a great portion of results for a certain element are close to the LOD this element was excluded from the modelling work.

Final elemental variables

Na

Mg

Al

Ca

Fe

Zn

Ba

Cu

Pb

Sr

Ti

V

ICP-OES

B, S, K, Mn: Results omitted due to the large portion of results that were below the LOD.

Results for Si omitted due to contamination problems.

ICP-MS

No results were reported for As, Cd, Cr, Hg or Ni since a large portion of results were below or only marginally above the LOD

Other elements were discarded for modelling reasons (P, Cu and Co, Nb, Zn and Zr, respectively)

NIR and visible reflectance
(NIR = Near Infrared Reflectans)

The utilization of NIR spectrometry for the present purpose is outside the traditional use of the technique.

The main use of NIR is determination of organic animal nutrition factors in feeds and forages and to a lesser extent in human food.

The instrument used here covers the visible range in addition to the near infrared part of the electormagnetic spectrum i.e. from 400-2500 nm. This was probably helpful since our soil samples were strongly coloured.

Information from reflectance spectra

Here we only want to use the spectral data to trace a compound spectrum of contributions from individual source materials.

In other words, we don´t have to know what chemical compounds are contributing to the spectra nor their concentrations.

The essence here is that spectral contributions form all compounds in all relevant sources will add up (linearly if the decomposition on the filter is not to great) to give a final NIR/vis. spectrum.

NIRS measurements

- *Instrument:*   *Foss NIRSystems, Model 6500*

- *Sample cups:*   *Circular, i.d. 38 mm, with quartz windows*

- *Wavelength range I:*   *400 - 1100 nm (visible)*

- *Wavelength range II:*   *1100 - 2500 nm (near infrared)*

- *Resolution:*   *2 nm both ranges (Total of 1100 data points)*

- *Filters*   *(37mm diameter) fastened with o-rings within sample cups.*

- *Reflectance is recorded as log[1/ I_R]*

- *Spectra reduced to 10 "points" through smoothing and averaging*

Background correction through blank subtraction is problematic here

- An inherent problem with reflectance spectra is the lack of a suitable zero reference or blank.

- Teflon filter membranes produce reflectance. Subtracting a blank (teflon) spectrum often gives negative spectra as the reflectance from the filter is to some extent replaced by analyte reflectance after collection of a dust sample i.e. the dust shields or masks some portion of the teflon surface.

Introduction of shielding coefficients, k_i

For a mixture of components, with known background shielding contributions, captured onto the filter surface, each point of the background spectrum is produced by a factor r < 1, calculated by the following expression.

$$r = \sum (k_i / m) * x_i \,, \qquad \text{where the sum is taken over all components (source materials)}$$

x_i is the mass fraction of a source and m is the total mass of collected material.

Calculation of shielding coefficients

- The k_i values for the different source materials were obtained from duplicate or triplicate spectra recorded from filters covered with different amounts of the same material (source).

- In essence, one calculates reflectance constants (reflectance signal divided by amount of source material on filter) for all measured wavelengths for a material and minimizes their differences (sum of squares) between samples by manual variation.

NIR/vis. spectra
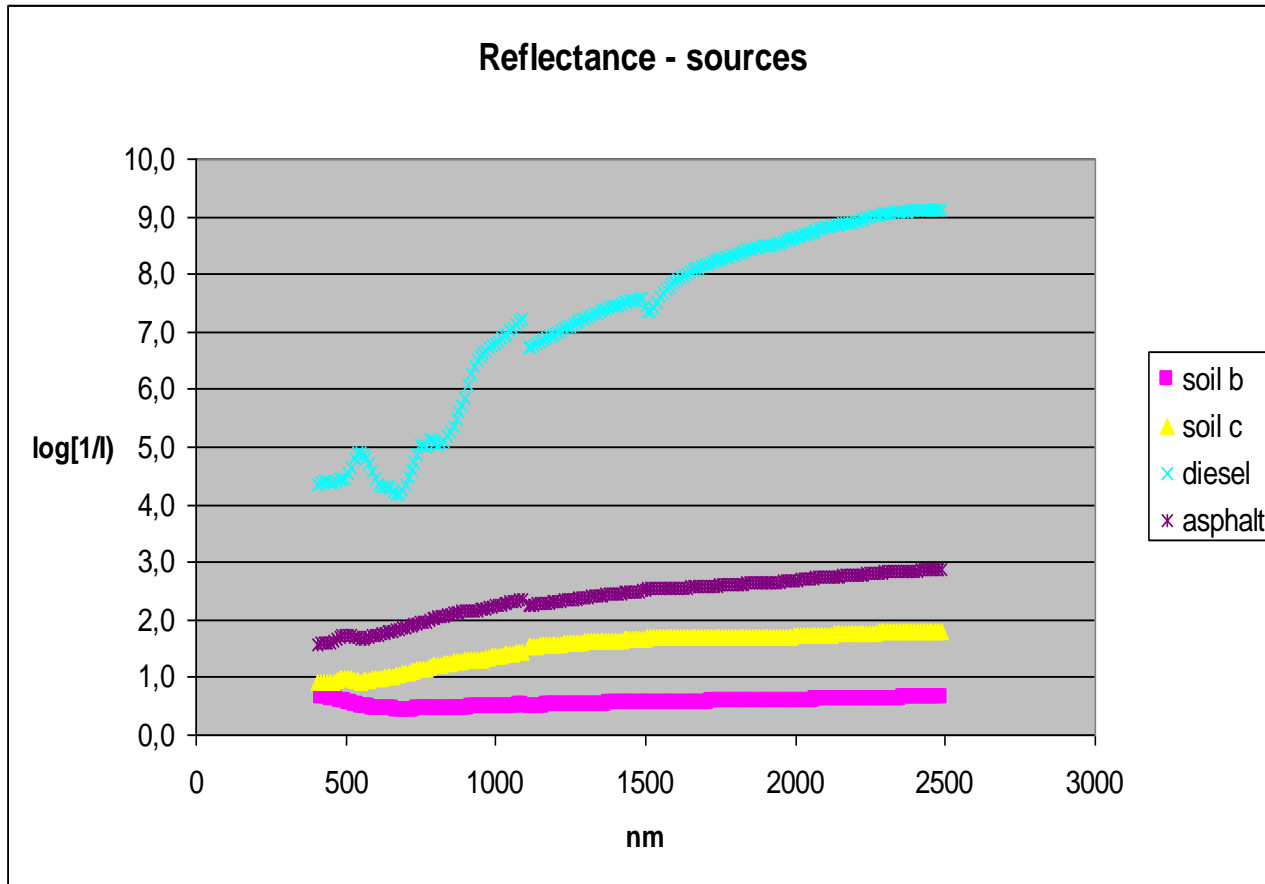
Blank-corrected signals from 1.0 mg of each source

Multivariate modelling

Chemometric software: *SIRIUS, Pattern Recognition Systems, Norway.*

Data pre-treatment: *Visual Basic program for pretreatment and smoothing of reflectance data*

                                     MS Excel for averaging and shielding calculations.

Modelling was done by Partial Least Squares regression or PLS

Using variables with varying numeric levels requires normalization.
Here, block normalisation was used, dividing each concentration value by the sum of values obtained for all the samples for the analyte in question.

Iterative procedure

Background shielding depends on the mass fraction of individual sources which in turn are the outcome of the model. That is, one needs a model results to calculate shielding and vice versa.

This was solved by guessing starting values for the composition of source materials. These were used to calculate initial shielding effects which in turned are used to calculate a PLS model. The resulting model values are then used to calculate new shielding effects and so on. Five rounds of iteration were needed.

Iteration, continued

The above mentioned tactic was used for the <2.5 µm fraction

The final modelling result for the <2.5 µm fraction was then used as a starting point for an iterative procedure for samples containing the "coarse" particles (<10 µm fraction).

Model results (<2.5 μm)

mg	Sample	Soil Predict	Asphalt Predict	Exhaust Predict	Salt Predict	Total %
0,35	3054F	0,09	0,36	0,30	0,24	99
0,24	3069F		0,43	0,42	0,15	100
0,12	3392F		0,12	0,76	0,07	95
0,09	3294F	0,11	0,42	0,44	0,08	105
0,10	3371F			0,91		94
0,89	3388F	0,23	0,70			93
0,12	3578F		0,62	0,35	0,07	104
0,10	3580F	0,07	0,45	0,33	0,07	92
0,22	3581F	0,30	0,42	0,22		94
0,13	3594F	0,41		0,36	0,16	95
0,20	3593F	0,06	0,21	0,41	0,22	90
0,36	3602F	0,36	0,43	0,06	0,09	94
0,17	3603F	0,07	0,41	0,37	0,09	94
0,09	3604F		0,50	0,40	0,12	102
	AVG(%)	0.12	0.37	0.38	0.11	97

Model results (<10 μm)

Sample	Soil Predict	Alphalt Predict	Exhaust Predict	Salt Predict	Total %
3069G	0,32	0,49	0,05	0,16	**102**
3294G	0,47	0,32	0,47	0,16	**141**
3392G	0,33	0,41	0,23	0,16	**112**
3409G	0,33	0,58	0,09	0,08	**108**
3371G		0,98			**98**
3388G	0,27	0,54		0,16	**97**
3578G	0,31	0,60		0,08	**99**
3580G	0,37	0,52	0,20	0,07	**117**
3581G	0,29	0,62		0,07	**98**
3593G	0,32	0,43		0,22	**96**
3594G	0,32	0,30	0,19	0,28	**109**
3602G	0,33	0,53	0,07	0,11	**105**
3603G	0,27	0,62		0,09	**99**
3604G	0,31	0,47	0,06	0,19	**103**
AVG	**0,33**	**0,53**	**0,12**	**0,14**	106

Concluding remarks

Considering the diversity of the raw data (macro and micro elements plus chemically undefined NIR/vis. variables) the results are rather good.

Contributions (percentage mass fractions) from each suspected source are modelled separately and then added to give a total, surprisingly close to 100% indicating that this is a valid methodology.