Supplemental Material

Source-specific fine particulate air pollution and systemic inflammation in ischemic heart disease patients

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Source Apportionment of $PM_{2.5}$ using EPA PMF 3.0

We determined the sources of fine particles ($PM_{2.5}$; particles with aerodynamic diameter less than 2.5 µm) by using U.S. Environmental Protection Agency's model EPA PMF 3.0. PMF (Positive Matrix Factorization) is an advanced multivariate receptor modeling technique that calculates site-specific source profiles and source contributions (Paatero 1997). Investigators comparing results of several source apportionment methods, including PMF, concluded that the results were consistent across users and methods (Hopke et al. 2006). One benefit of PMF compared to other methods is point-by-point scaling of the data that enables PMF to handle missing and below-detection-limit data that commonly occur during environmental measurements. The U.S. EPA's Office of Research and Development has developed a stand-alone graphical user interface (EPA PMF 3.0) that is freely distributed (Norris et al. 2008).

EPA PMF 3.0 solves the general receptor model using constrained, weighted least-squares as implemented in the program ME2 (Multilinear Engine) (Paatero 1999). The mathematical equation for the model is

$$x_{ij} = \sum_{p=1}^{P} g_{ip} f_{pj} + e_{ij} \quad \begin{pmatrix} i = 1, ..., I \\ j = 1, ..., J \\ p = 1, ..., P \end{pmatrix} \tag{1}$$

where x_{ij} is the j^{th} species concentration measured in the i^{th} sample, g_{ip} is the particulate mass concentration from the p^{th} source contributing to the i^{th} sample, f_{pj} is the j^{th} species mass fraction from the p^{th} source, e_{ij} is residual associated with the j^{th} species concentration measured in the i^{th} sample, and P is the total number of independent sources.

The task of EPA PMF is to minimize the sum of squares

$$Q = \sum_{i=1}^{I} \sum_{j=1}^{J} \left(\frac{x_{ij} - \sum_{p=1}^{P} g_{ip} f_{pj}}{\sigma_{ij}} \right)^2 \qquad (2)$$

The value σ_{ij} is the uncertainty of the measured value x_{ij}. We constrained all sources to have non-negative species concentration, and allowed no sample to have negative source contribution. We operated the model in a robust mode so that for any data point for which the residual exceeded 4 times the error estimate, the value was processed as an extreme value and its weight was decreased.

The use of point-by-point error estimates as the weight of the data points improves the fit since more accurate values get more weight than less accurate values. Thus, the accuracy depends on the analyzed species as well as on its concentration level. We determined the uncertainty as

$$\sigma = \begin{cases} 2 \times \mathrm{MDL}, \text{if concentration} \le \mathrm{MDL} \\ \sqrt{(\text{percentage} \times \text{concentration})^2 + (\mathrm{MDL})^2}, \text{if concentration} > \mathrm{MDL} \end{cases} \qquad (3)$$

where MDL was the method detection limit. For ions and levoglucosan we used MDLs based on the chemical analysis. For other composition data, we estimated the values from the lowest reported concentrations. The percentage uncertainty consists of the analytical reproducibility and the modeling uncertainty. Modeling uncertainty is included, because data do not exactly meet the modeling assumptions, namely the assumption that the ratios of species in each factor do not vary through time (Norris et al. 2008). We used 20 percent as the modeling uncertainty, which produced reasonable relative uncertainties for each dataset.

We measured and collected $PM_{2.5}$ samples at urban background station between 14 Nov 2005 and 21 Apr 2006. In the model, we used daily average concentrations of $PM_{2.5}$, absorption coefficient (ABS), particle number concentration (PNC), as well as sodium (Na^+), ammonium (NH_4^+), potassium (K^+), magnesium (Mg^{2+}), calcium (Ca^{2+}), chlorine (Cl^-), sulfate (SO_4^{2-}) and oxalate ions, and levoglucosan. In addition, we utilized NO concentration measured at a nearby (450 m) municipal measurement site. Number of data points, geometric mean, geometric standard deviation, and MDL are presented in Table S1. In the data, we substituted missing values with geometric mean and weighted them down by four ($\sigma_i=4\sigma_i$).

Source Apportionment Results

We run the model with 4 to 10 factors from 100 random starting points. We regarded the five factor model as the best solution to interpret the likely sources. Correlation coefficients between source categories and the individual pollutants are presented in Table S2 (Supplemental Material, Table S2).

The first factor contained high percentages of SO_4^{2-} and NH_4^+ concentration (Supplemental Material, Figure S2). Also oxalate was associated with this factor. SO_4^{2-} and NH_4^+ ions are common tracers of secondary aerosol PM, which is formed from inorganic and organic gaseous emissions during regional transport within hours or maybe one day or during long range transport (LRT) of air masses for hundreds of kilometers within some days. Oxalate can originate from primary emissions of biomass burning (Yamasoe et al. 2000) and/or be formed as a secondary product by the oxidation of gaseous organic compounds (Kawamura and Ikushima 1993). The average source contribution of LRT to $PM_{2.5}$ was 4.5 µg m^{-3} or 56% (Supplemental Material, Table S3). The highest concentrations took place between the end of February and mid-March (Supplemental Material, Figure S3).

The factor describing traffic emissions was characterized by NO and PNC, and to lesser extend by Ca^{2+} and ABS (Supplemental Material, Figure S2). Emissions from gasoline and diesel powered vehicles could not be separated from each other on the daily level. Ca^{2+} indicates that also traffic induced road dust emission was included in this factor, in addition to the tailpipe exhaust emissions. Traffic emissions explained, on average, 8% of the $PM_{2.5}$ mass (Supplemental Material, Table S3). Contribution of traffic emissions was higher during weekdays than weekends.

The third factor explained 96% of the variation in levoglucosan concentration. Levoglucosan is a commonly used, specific and relatively stable organic chemical tracer for biomass combustion that is exclusively produced by thermal breakdown of cellulose and diverse hemicelluloses (Simoneit 2002). Other, non-specific tracers of biomass burning include black carbon and ions such as K^+ from inorganic ash, and oxalate. In our data, also ABS and K^+ were associated with this factor. Thus, this factor described $PM_{2.5}$ emissions from biomass combustion. The average source contribution was 1.6 µg m^{-3} (20%) (Supplemental Material, Table S3).

The fourth factor described the sea spray aerosols. It explained 90% of the variation in Cl^- concentration and the ratios of the sea salt components, i.e. Cl^-, Na^+, SO_4^{2-}, Mg^{2+}, K^+ and Ca^{2+}, were close to that in sea water. Sea salt particles were observed in Kotka when the air masses had passed over the Northern Atlantic before arriving to the measurement site (data not shown).

Almost 70% of the Na^+ concentration and 20-30% of Ca^{2+}, K^+ and Mg^{2+} concentrations were associated with the fifth factor. The highest concentrations (Supplemental Material, Figure S3) were observed during northern winds and back trajectories arriving via south-east border of Finland (data not shown). There are several pulp mills in Kotka and near the border within 140 km from Kotka. All of these facilities used sulfate process for conversion of wood into wood pulp. The electric filters used to control the emissions enable high efficiency particulate removal, but some emissions of Na^+, SO_4^{2-} and Ca^{2+} (and K^+) are possible (Wahlberg H, personal communication). Although the average $PM_{2.5}$ concentration corresponding to this factor was low, levels as high as 4-6 µg/m³ were observed on some days. On average, $PM_{2.5}$ components from pulp mills formed 13% (1.0 µg/m³) of the $PM_{2.5}$ mass.

Correlation between the measured $PM_{2.5}$ and the sum of source-specific $PM_{2.5}$ was very high (R^2=0.95).

Limitation in the source apportionment was the lack of daily concentrations of V and Ni, tracers for residual oil combustion emissions from port and ship traffic. The port of Kotka is a major sea port in Finland, and thus emissions from ships burning No. 6 fuel oil are likely to contribute to the urban $PM_{2.5}$ concentration. According to the SPECIATE 3.2 speciation profile for uncontrolled residual oil combustion the weight fraction of Vanadium in $PM_{2.5}$ is 3.44% (http://cfpub.epa.gov/si/speciate/ehpa_speciate_browse_details.cfm?ptype=PD&pnumber=135012.5, 8.8.2014). In Kotka, V and Ni, among other metals, were analyzed from four-day (from Monday to Friday) samples collected with virtual impactor. The average V concentration was 5.0 µg/m³ while Ni concentrations were mainly below the quantification limit. Based on V concentration, a rough estimation on contribution of ship emission to $PM_{2.5}$ in Kotka is 0.1

μg/m³. Without the tracer elements, these emissions are likely to be combined with traffic emissions, the other local fossil fuel combustion source.

Daily concentrations of tracers for airborne soil (Si, Al, Fe) were not available. However, during the cold season, contribution of airborne soil can be estimated to be low. Aurela et al (2010) reported that based on chemical mass closure of four-day samples, soil-derived material accounted for 3% ± 2 % of the $PM_{2.5}$ mass in Kotka.

The model was stable and the identified source categories are known to be present in Kotka. Furthermore, the composition and temporal variation of the factors were physically reasonable. Addition of data on metal and organic marker species would enable separation of other minor sources.

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Supplemental Material, Table S1. The number of data points above minimum detection limit (MDL), geometric mean (GM), geometric standard deviation (GSD), and MDL for variables used in the present source apportionment model.

	N	GM	GSD	MDL	UNIT
$PM_{2.5}$	130	7.5	2.1	0.5	µg m^{-3}
ABS	128	1.3	1.9	0.1	10^{-5} m^{-1}
NO	115	18	1.7	1.0	µg m^{-3}
PNC	128	5284	2.0	500	cm^{-3}
Na^+	130	109	2.1	2.0	ng m^{-3}
$NH4^+$	130	561	2.6	2.0	ng m^{-3}
K^+	130	63	2.2	2.0	ng m^{-3}
Mg^{2+}	130	6.4	2.1	2.0	ng m^{-3}
Ca^{2+}	130	23	2.0	2.0	ng m^{-3}
Cl^-	130	16	3.1	2.0	ng m^{-3}
$SO4^{2-}$	130	1883	2.2	2.0	ng m^{-3}
Oxalate	130	31	2.9	1.0	ng m^{-3}
Levoglucosan	123	29	3.1	1.0	ng m^{-3}

$PM_{2.5}$ = particles less than 2.5 µm in aerodynamic diameter;

ABS=absorption coefficient

PNC = particle number concentration

Supplemental Material, Table S2. Correlation coefficients between source categories and the individual pollutants.

	LRT	Traffic	Biomass	Sea salt	Pulp mills
ABS	**0.57**	0.41	**0.80**	-0.31	0.35
NO	0.33	**0.66**	0.47	-0.05	0.25
PNC	0.21	**0.62**	0.14	-0.17	0.25
Na$^+$	-0.04	0.04	0.02	0.39	**0.82**
NH4$^+$	**0.97**	0.12	**0.64**	-0.37	0.14
K$^+$	**0.53**	0.25	**0.73**	-0.21	**0.54**
Mg^{2+}	-0.26	-0.16	-0.16	**0.67**	0.23
Ca^{2+}	0.15	0.45	0.34	-0.01	**0.70**
Cl$^-$	-0.39	-0.08	-0.18	**1.00**	-0.06
SO4^{2-}	**0.88**	0.06	**0.53**	-0.38	0.23
Oxalate	**0.77**	0.01	**0.70**	-0.35	0.01
Levoglucosan	**0.58**	0.15	**0.97**	-0.20	0.18

ABS=absorption coefficient

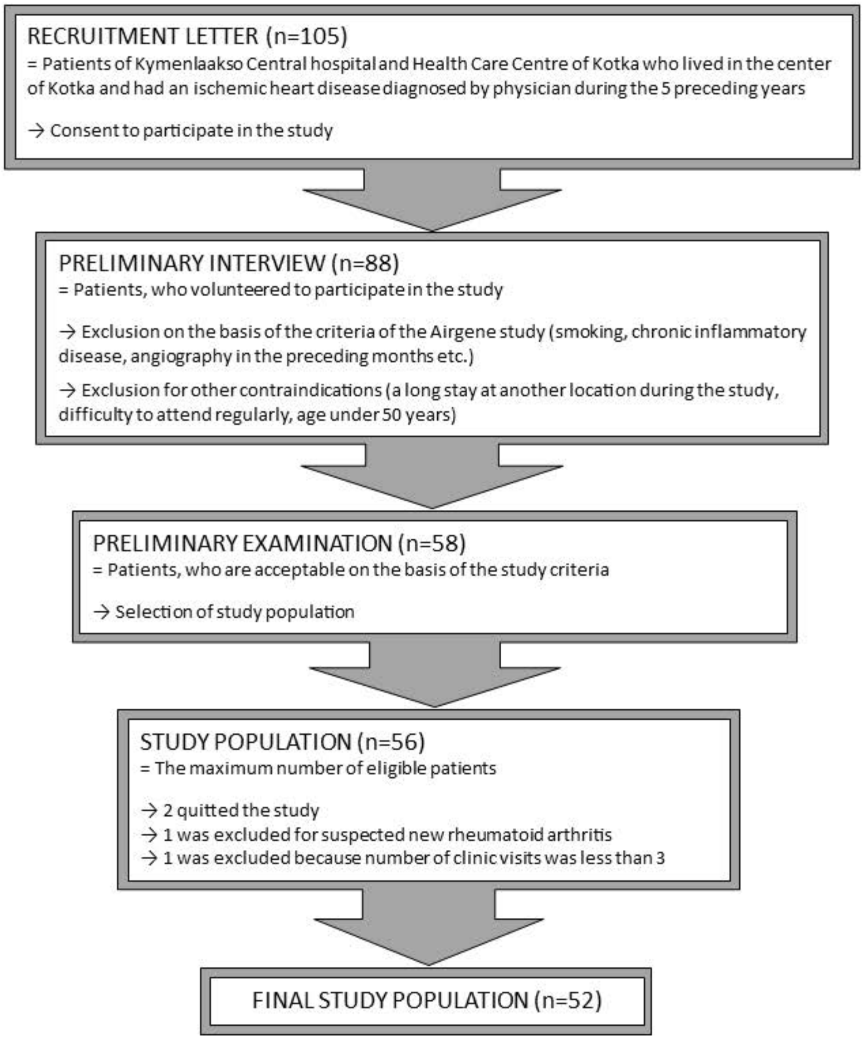
PNC = particle number concentration

Supplemental Material, Table S3. The average mass contributions of identified sources to $PM_{2.5}$ mass.

	$PM_{2.5}$ (µg m^{-3})	$PM_{2.5}$ %
LRT	4.5	56
Traffic emissions	0.6	8
Biomass burning	1.6	20
Sea salt	0.1	1
Pulp mills	1.0	13

$PM_{2.5}$ = particles less than 2.5 µm in aerodynamic diameter;

LRT = regional and long range transport



RECRUITMENT LETTER (n=105)
= Patients of Kymenlaakso Central hospital and Health Care Centre of Kotka who lived in the center of Kotka and had an ischemic heart disease diagnosed by physician during the 5 preceding years

→ Consent to participate in the study

PRELIMINARY INTERVIEW (n=88)
= Patients, who volunteered to participate in the study

→ Exclusion on the basis of the criteria of the Airgene study (smoking, chronic inflammatory disease, angiography in the preceding months etc.)

→ Exclusion for other contraindications (a long stay at another location during the study, difficulty to attend regularly, age under 50 years)

PRELIMINARY EXAMINATION (n=58)
= Patients, who are acceptable on the basis of the study criteria

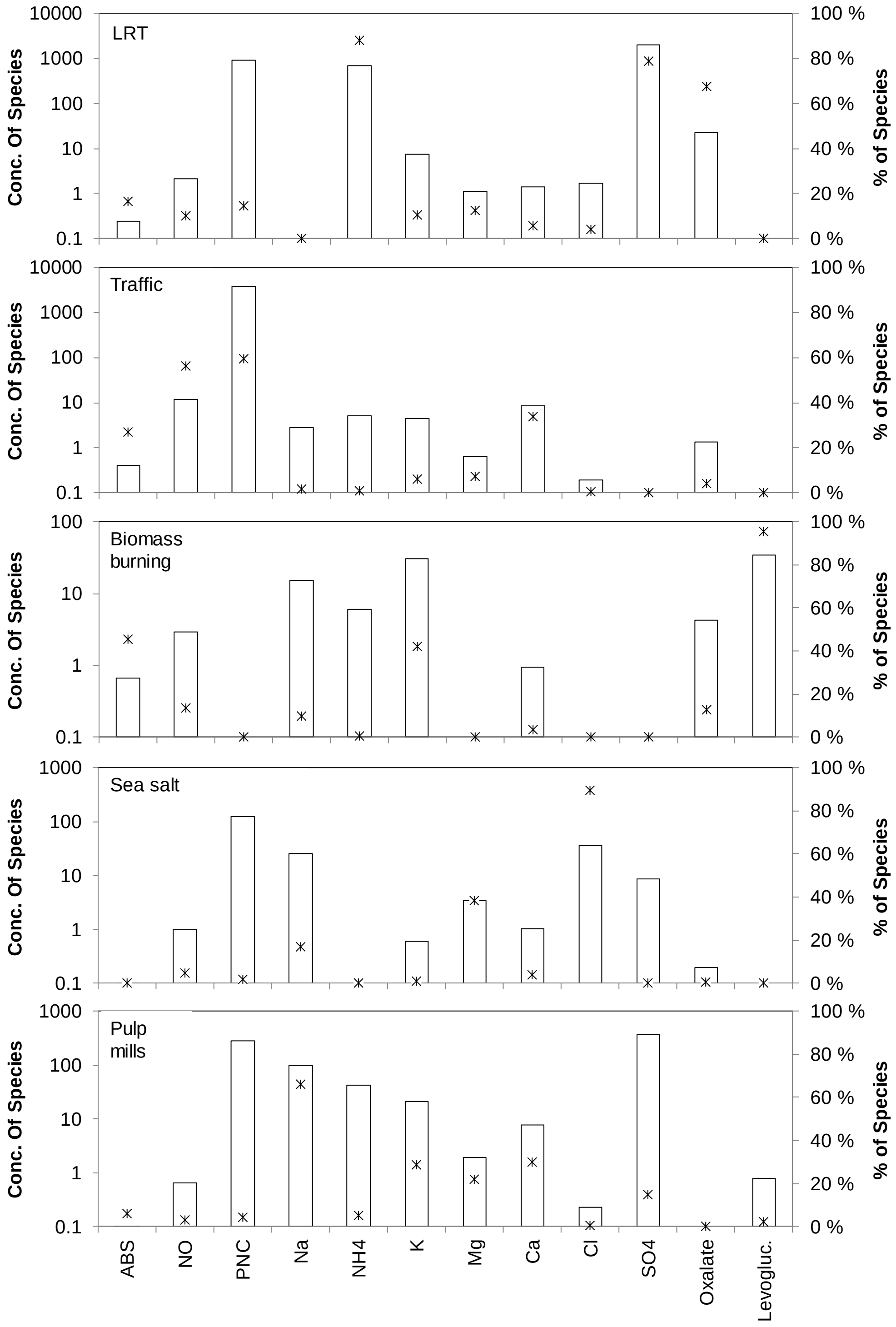
→ Selection of study population

STUDY POPULATION (n=56)
= The maximum number of eligible patients

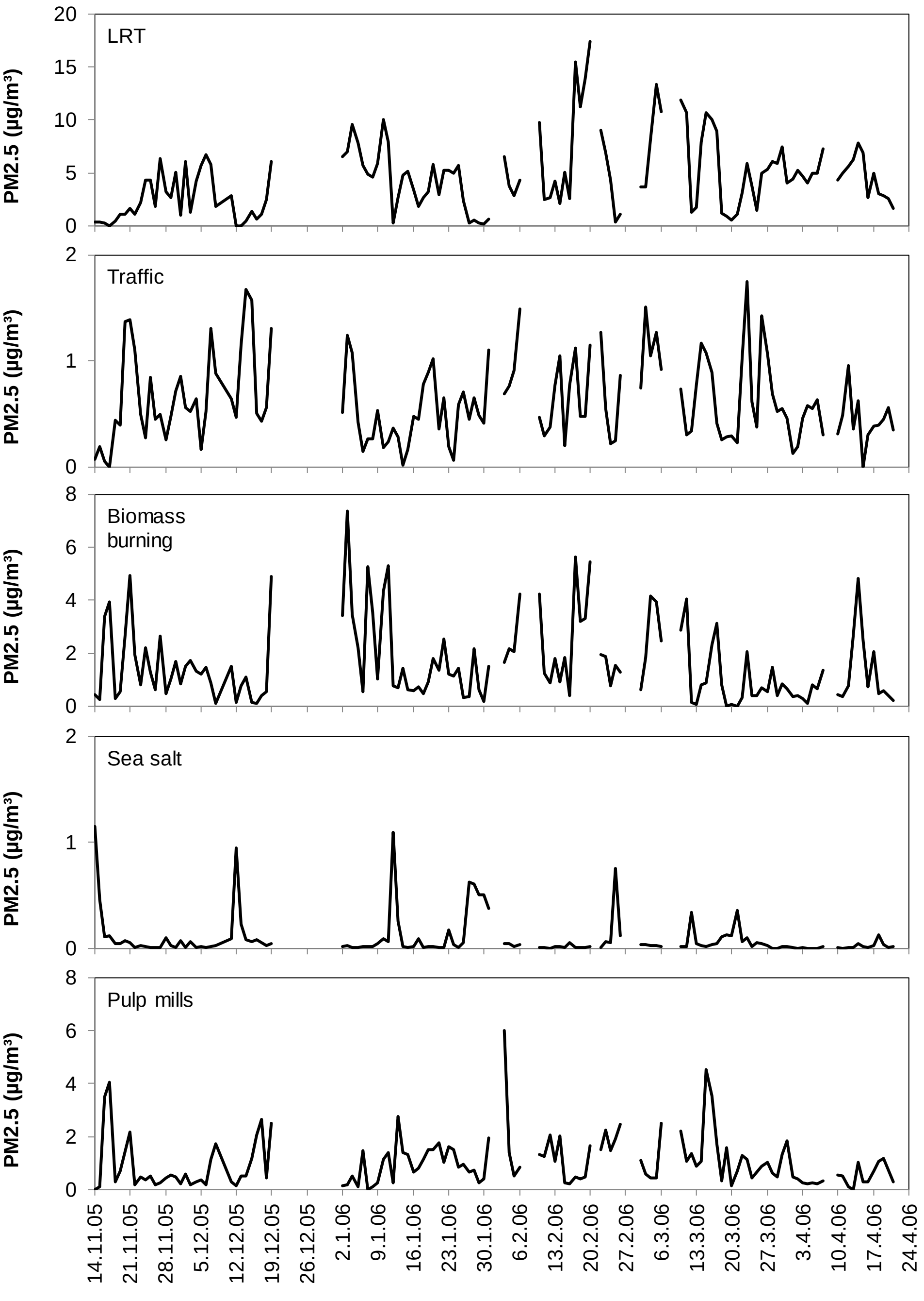
→ 2 quitted the study
→ 1 was excluded for suspected new rheumatoid arthritis
→ 1 was excluded because number of clinic visits was less than 3

FINAL STUDY POPULATION (n=52)

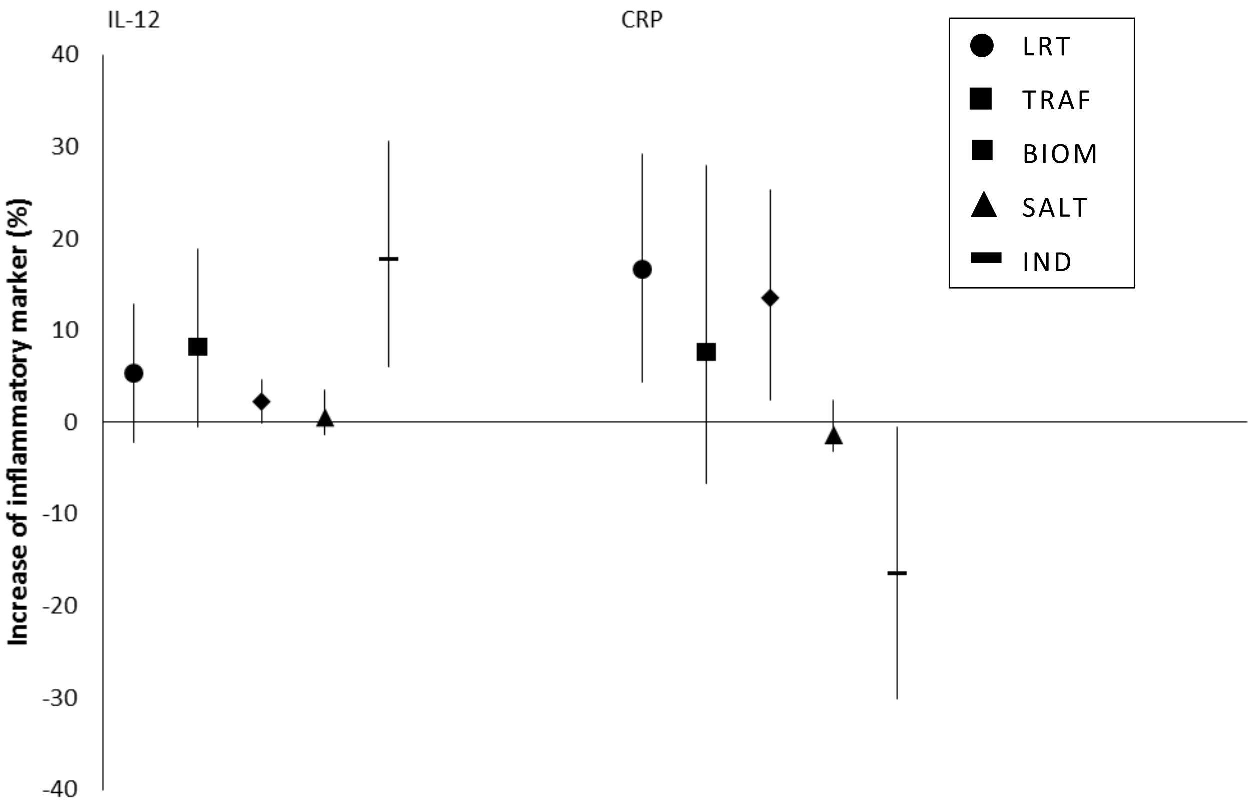
Supplemental material, Figure S1 Recruitment process.



Supplemental Material, Figure S2. Factor profiles in Kotka. Columns = concentrations of species (units in table S1); * = relative contribution of resolved factors to chemical species (%). (LRT = regional and long range transport)



Supplemental Material, Figure S3. Source-specific contributions to daily $PM_{2.5}$ in Kotka. (LRT = regional and long range transport)



Supplemental material, Figure S4 Estimated effect of 5-day average source-specific $PM_{2.5}$ (particles smaller than 2.5 µm in aerodynamic diameter) on interleukin-12 (IL-12) and C-reactive protein (CRP). Effect estimates have been calculated as percent changes of the outcome mean per interquartile increase in air pollution concentration together with 95-% confidence intervals. (LRT = regional and long-range transport; TRAF = traffic emissions; BIOM = biomass combustion; SALT = sea salt; IND = pulp industry).