

AEROSOL-BORNE TRACE ELEMENTS IN BULGARIA: CONCENTRATION LEVELS IN COASTAL AND MOUNTAINOUS REGIONS

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Abstract. Much knowledge is lacking with respect to atmospheric trace-element concentrations in Bulgaria. We here report from a study of aerosol-borne concentrations of Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ge, As, Se, Br, Rb, Sr, Zr, Mo, Cd, Hg, Ag, and Pb in the southern Bulgarian Black Sea region and in the high-elevation Rhodope and Rila mountains. Our findings are novel for these regions. Time-weighted concentration levels (ng m^{-3}) at the coastal site were for S, Si, Ca, Cl, Fe, and K in the range 100 to 1000; Zn, Al, Br, P, and Ti 10 to 100; Pb, Mn, V, Cu, Cd, Ag, and As 1 to 10; while Zr, Cr, Ni, Hg, Co, Se, Rb, Zr, Mo, Ge, and Ga were below 1. S, Cl, V, Zn, and Se levels were higher at the coastal site (Cl by a factor 20). Si, Ca, Cl, Fe, Al, Ti, and Sr were coarse-fraction oriented, and S, Zn, P, Pb, V, As, and Se fine-fraction oriented, at the coastal site. Similar features characterised the mountain sites; however, Cl and K at the Rila mountain site were fine-fraction dominated, Zn at the Rhodopes site was coarse-fraction oriented. We compare our findings with results from other studies in marine and mountain environments, and with general ranges commonly used to indicate whether regions are of remote, rural, or urban type. Levels found at our sites fall in the categories "remote" and "rural"; in some cases (Co, Ni, Cd, Hg) "urban". Our results hold opportunities for source-region identifications and for input to deposition models. However, substantial further research is needed to assess these and other pressing problems with Bulgarian air quality and forest vitality.

Keywords macro and micro-constituents, heavy metals, Black Sea, Rila and Rhodopes Mountains

Introduction

Trace elements in forest ecosystems have been intensively studied during the past decades (e.g., Wiman and Lannefors, 1985; Wiman et al., 1990; Fowler, 1992; Johnson and Linberg, 1992; Lindberg and Owens, 1993; Erisman and Draaijers, 1995; Draaijers et al., 1997a,b; Arends et al., 1997; Seinfeld & Pandis, 1998; Erisman and Draaijers, 2003). In several forest-rich countries, however, including Bulgaria, opportunities have not been favourable with respect to launching and carrying through biogeochemistry and air pollution programmes of the type needed (Bytnerowicz, 1992; Zeller et al., 1997; Bussotti and Ferretti, 1998). In addition, the needs for obtaining trace element concentration data in forest atmospheres are now being placed in the perspectives of climatic changes, manifesting themselves as shifts in meteorological parameters (e.g., Wiman, 2002; Karnosky et al., 2003; Bodin and Wiman, 2007). Such shifts may affect the importance of aerosol vis-à-vis precipitation physico-chemistry. Also, trace-element concentration data from relatively remote or rural regions can assist as references in assessments of urban pollution and related effects on human health (cf., Houthuijs et al., 2001). In order to help improve the Bulgarian information base the project "Integrated Environmental Diagnosis and Assessment of ecological systems at risk in Bulgaria" (IEDA) was initiated in 1998 to investigate a range of biogeochemistry and biogeophysics forest systems components of low-elevation coastal-zone oak forests and high-elevation montane pine forests (cf., Syrakov et al., 1998; Wiman et al., 1999a,b; Wiman et al., 2002; Gaydarova, 2003; Wiman and Gaydarova, 2008). The project, now in its data synthesis phase, includes long-term (month-by-month) data sampling as well as intense and short-duration field efforts. In the current contribution we focus on data now available from the project's long-term aerosol sampling programme 1998-2000.

Sites and Methods

The Ahtopol, Rozhen, and Malyovitsa sites

We obtained aerosol data in three regions in Bulgaria: the southern Bulgarian Black Sea coastal forest region (Site C), the Rhodopes (Site R), and Rila (Site M) mountains; cf. Fig. 1. The project's Site C is in the Strandzha area along the Black Sea. For the long-term sampling reported on here we used a location situated 2 km south of the small town of Ahtopol and about 200 m from the shoreline. The area is part of a vast coastal high-biodiversity forest aggregate (dominated by *Quercus frainetto* Ten.) and covers altitudes up to about 200 m above sea level (asl). The climate is mild, with a Mediterranean influence. The region is poorly studied with respect to biogeochemistry, and, having earlier been closed to public access, is now subjected to rapid urbanisation.

The Rozhen site (R; 1650 m asl) is a Scots pine enclave located in a *Piceta abies* formation in the Rhodopes. The area is characterized by transitional continental and transitional Mediterranean regimes. Site R is situated on a gentle mountain top in the vicinity of an astronomy observatory run by the Bulgarian Academy of Sciences. Site M (in the Malyovitsa area; 1650 m asl) is located in the highest-elevation region of the Balkan

peninsula, the Rila mountains, and holds a vast coniferous forest area dominated by *Pinus sylvestris* L. The Malyovitsa area is characterized by relatively short summers and cold winters with long-lasting snow cover.

A range of meteorological parameters, including wind velocity, were obtained in our own measurements at the three sites. Details cannot be accommodated here, but confirm the existence at Site C of a typical spring and summer local circulation with stronger sea-to-land winds during the day from NE and weaker SE winds at night (land-to-sea) (cf., Kallos et al., 2000; Skakalova et al., 2003). During winter there are stronger winds from SW and N. Our measurements at Site M were consistent with earlier assessments of the wind-valley circulation system in the area (Donev et al., 1998). To some extent, and in analogy with the wind circulation system in the Site-C region, aerosols can be expected to become partly trapped in circulating air-masses. On days with strong synoptic flows in the Malyovitsa area, the diurnal mean wind direction usually varies from S to W. The Rozhen site does not experience a local wind circulation, due to its mountain-top location. There is thus basis to assume that wind regimes at Rozhen to a large extent represent general regional conditions on a scale probably up to some 100 km or more whereas the Malyovitsa measurements to a substantial degree exemplify fairly local conditions (about 10 km scale) of topography and forest complexity. For Site R, our data show that the largest volume of air enters Site R from the W-to-N sector. This implies that the physico-chemistry of aerosol particles smaller than a few μm would be more strongly influenced by such air-masses. However, this does not necessarily mean that the most influential sources should be sought in that sector because of long-distance transports and aerosol formation processes occurring along complex trajectories in the atmosphere (e.g., Lammel et al., 2003). More detailed ecological descriptions of the sites, in particular for Site C, are given in Gaydarova (2003) and Wiman and Gaydarova (2008); in regard to climatology see also Nikolov and Jordanova (1997).

The sites in relation to the Bulgarian air-pollution geography

Detailed and quality-assessed information on Bulgarian emissions of air pollutants is scarce. However, a brief overview of the situation can be made. Total SO₂ emissions from Bulgarian sources in 2001 amounted to ca 1 Mt (Todorov, 2002; BNSI, 2003) with a possibly downward (but slow) long-term trend (BMEW, 2001; Todorov, 2002). The biggest point sources of SO₂ pollution in Europe are the Maritsa and Maritsa North thermal power plants (Barret, 2000) (situated about 250 km E of our Malyovitsa site) which in 2002 together emitted 0.6 Mt of SO₂. Sources with industrial and traffic emissions of importance to the mountain sites are the city of Plovdiv (about 50 km N of the Rozhen site and about 150 km east of Malyovitsa) and the capital Sofia (about 60 km N of Malyovitsa and about 150 km NW of Rozhen). In 2001, 0.042 Mt of SO₂ were emitted from the Bourgas area (BNSI, 2003) about 100 km N of Site C. Together with the Bourgas region, Pomorie and Yambol (about 200 km to the NW) are the main pollution source-areas in the coastal region (chemical industries, shipping; cf., Kallos et al., 2000) which is also subject to increasing tourism-related traffic. H₂S emissions in the area emanate from the Black Sea in addition to industrial sources, including the Bourgas oil refinery (Teneva et al., 1986).

In a study of sediments from the Varna and Bourgas coastal regions, Simeonov et

al. (2000) define the Bourgas gulf as heavily polluted with Cu, Pb, Mn, Zn, Co, Cd, Cr, Fe, Ni, and As. This is a general indicator of the environmental quality situation in Bulgaria with respect to heavy metals. In terms of Bulgarian emissions to the atmosphere, 317 t of Pb, 8.4 t of Cd, 6.9 t of Hg, 10.2 t of As, 20.8 t of Cu, 177 t of Ni and 219 t of Zn were released in 1990 (EEA, 1998). Bulgarian emissions of Pb, Cd, and Hg to the atmosphere were, in 2005, 115, 12, and 3.4 t, respectively (data for other metals are lacking) (EEA, 2007). The latter emissions account for around 5%, 10%, and 4% of the total (reported) EU27 emissions of Pb, Cd, and Hg.

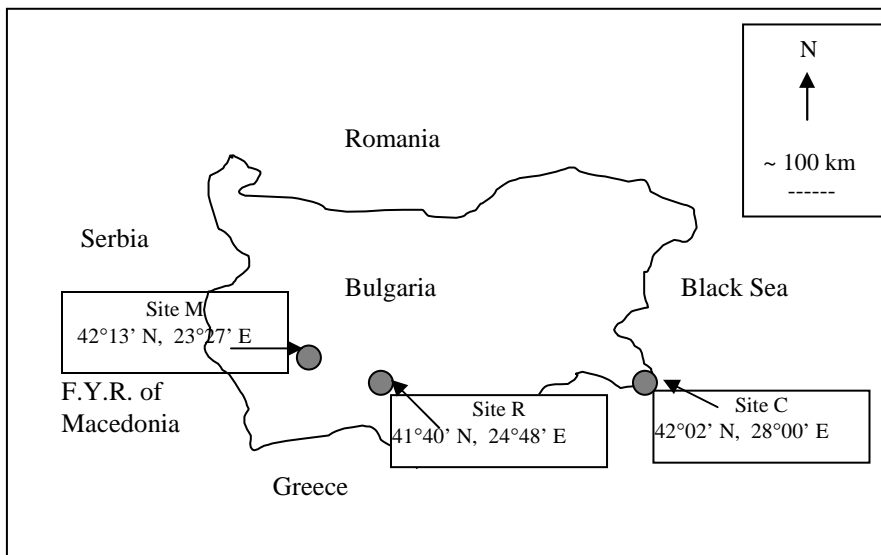


Fig. 1. Geographical location of the Ahtopol (C), Rozhen (R) and Malyovitsa (M) sites.

Aerosol sampling, analysis and data processing

The atmospheric aerosol was sampled with a Nuclepore 2-stage filter system using 8 μm pore-size, 25 mm diameter filters for coarse particles; and 0.4 μm pore-size, 25 mm diameter filters for fine particles. At Site C, the sampler was positioned on a 4 m tall mast placed on the rocky (ca 10 m asl) shore 200 m W of the Black Sea. Pump and power supplies were placed inside a building 10 m NW of the mast. The Site R sampler was positioned at 2 m above the ground and 1 m away from a small sampling cabin on the open mountain top, with pump and power supply arranged inside the cabin. The sampler at Site M had to be positioned inside the forest, with the sampler 1 m away from a suitable tree trunk and 2 m above the ground, and connected with pump and a battery (no mains available) in a container dug down in the ground soil. Sampling duration at all sites was around 1 month, but the loss of equipment and thus data was severe at Site M which was not possible to either secure sufficiently or access and run during the winter season. Usable

sampling periods at the respective sites are identifiable in Fig. 2.

Pumps used at all sites were of low-volume type with some ability to compensate for pressure drop caused by the successively increasing mass-load on the filters. Sampling flow rate was set to 1 litre per minute ($L \text{ min}^{-1}$) which at Site M typically decreased by about 40% over the about one month of sampling. At Sites C and R, logistics enabled sampling flow rates to be kept at 1 to $0.8 L \text{ min}^{-1}$. The filter holder set-up included the external lid, so as to safeguard against rain. Sampling was vertically upwards. The inlet of this lid has an inner diameter of 4.5 mm and an outer diameter of 8 mm, and extends 4 mm from the lid. The arrangement gives a 50% cut-off diameter for the coarse-particle filter at around $3 \mu\text{m}$ (cf., Heidam, 1981); in the following, we use the term "coarse fraction" for values obtained with the 1st filter stage and "fine fraction" for values obtained with 2nd stage. We note that Eleftheriades and Colbeck (2001) for a rural and an urban site found the mass concentration of particles $>10\mu\text{m}$ to be less than 10-15% of the total coarse-mode mass concentration for trace elements. This suggests that the part of the coarse mode presenting the greatest sampling difficulties is small enough not to invalidate our coarse-fraction data. The exposed Nuclepore filters were brought to PIXE analysis (cf., e.g., Johansson and Johansson, 1976; Lannefors, 1982) at the Department of Nuclear Physics, Lund University (Sweden) in sealed holders. After analysis and evaluation of X-ray spectra (courtesy of the PIXE group, Lund Institute of Technology at Lund University) resulting raw data were processed to provide concentrations.

The error calculation procedure addresses concentration C as given by $C = f(E, B, V)$, where E is the mass of the element on the exposed filter, B is the mass of the element in the blank-filter, V is the total air volume sampled through the filter. Differentiation structures C into partial errors of various types (PIXE analysis error, blank-filter corrections, integrated flow errors, and others) and these errors can be considered as discussed in Wiman and Lannefors (1985), so that the resulting concentration uncertainty ΔC_i , for period i , can be estimated for the various elements analysed. For establishing the average concentration levels (for coarse and for fine fractions) at the respective sites time-weighted concentration means were calculated (as $[\sum t_i (C_i \pm \Delta C_i)] / (\sum t_i)$, where t_i , C_i , and ΔC_i are, respectively, duration, concentration and concentration error of sampling period i). For calculations of the total (time-weighted) concentrations, coarse- and fine-fraction concentrations (time-weighted) concentrations were added, and the resulting error estimated from the square root of the sum of the squared time-weighted errors of coarse and fine fractions. For cases where no amount above the mean value of the blanks was detected on the exposed filters the sample concentration was assigned the one- σ blank value (15 blanks of each pore-size type were PIXE-analysed).

Results and discussion

Temporal concentration variations

We confine our presentation here to exemplifying results for the concentration variations of fine-fraction and coarse-fraction sulphur and chlorine (Fig. 2). S typifies long-distance transports in the fine (mainly anthropogenic) particle fraction whereas the coarse-

particle fraction can be expected to be fairly strongly influenced by near-regional and local sources. Cl has major marine aerosol sources (cf., e.g., Foltescu et al., 2005) but is also known to emanate from for example fossil-fuel combustion (via volatilization-condensation processes; e.g., Bowen, 1982). Fig. 2 shows a pronounced concentration variability for both these elements, in coarse as well as fine fractions. This reflects different air-masses, and their transport routes. Concentrations of coarse-fraction Cl at Site C are an order of magnitude above those recorded at the mountain sites. Occasionally, high fine fraction Cl-concentrations also occur at Site C, thus suggesting that the Black Sea can act as a source also for long-distance transports of elements from sea-surface micro-film bubble-bursting (cf., Wiman 2000). These and other patterns (such as occasionally quite high fine-fraction concentrations of S and Cl at Site R) in Fig. 2 suggest opportunities for further analysis of the relative importance of source regions of importance to the sites, through, *inter alia*, concentrations-versus-wind-sector studies (for approximate indications) (e.g., Lannefors, 1982; Swietlicki and Krejci, 1996), air-mass trajectory analysis (Wiman et al., 2002), or more advanced methods (Lammel et al., 2003). The analysis and discussion of source types (e.g., Bowen, 1982; Lannefors et al., 1983; Duce, 1983; Hardy et al., 1985; Wiman and Lannefors, 1985; Ross, 1985; Warneck, 1988; Davison and Hewitt, 1992; Andreae and Crutzen, 1997; Seinfeld and Pandis, 1998; Sander et al., 2003) can be expanded to include temporal concentration variations of further elements in our data set. However, the current contribution confines itself to discussing, in the next section, a few source aspects in relation to time-averaged levels.

Time-averaged mass concentration levels of elements, and coarse versus fine fraction tendencies

Total-concentration levels. Fig. 3 shows the time-averaged aerosol-borne mass concentration levels, by element and filter stage, and site-by-site, in a manner that indicates which fraction (coarse or fine) is the main mass-carrier of the element. The graph is organised to show elements as their average concentrations decline in the Site-C data set and categorised into four Site-C magnitudes (category a: concentrations 100 to 1000, b: 10 to 100, c: 1 to 10, and d: $< 1 \text{ ng m}^{-3}$). It should be observed that the available periods for Site M approximately cover a vegetation season (if measurements in 1988 and 1999 are combined) whereas Site-R data essentially cover a year and Site-C data about two years. Interpreting concentration differences between the three sites thus warrants caution in particular with respect to Site M, since the data set from that site is limited (with a lack of winter-season data) and since sampling at that site had to be carried out inside the forest (thus depleting the aerosol through sink processes; cf., e.g., Wiman and Ågren, 1985; Pryor 2006). However, a major feature in Fig. 3 is that total (fine plus coarse) Cl concentration at Site C is substantially higher than at the mountain sites (a factor of 20 and 7 for Site R and Site M, respectively), thus showing the significant marine influence on the coastal-forest biogeochemistry. Also, the S concentration is higher at Site C which likely indicates a combination of marine and anthropogenic sources (cf. section 2.1). Fig. 3 shows a higher average concentration of Zn at the coastal site (possibly explainable by resuspension, through bubble-bursting, of Zn enriched in the sea-surface microlayer; cf. e.g., Bowen, 1982) and a higher Al concentration at the mountain sites (likely to reflect soil sources). The

Br concentration value at Site C is, unfortunately, marred by high and variable background Br values in the filters tested for blank determinations with respect to the batch of $0.4 \mu\text{m}$ filters used for part of the coastal sampling. The coastal V concentration level stands out as high relative to the mountain levels (which reside on the $< 1 \text{ ng m}^{-3}$ level) and might emanate from anthropogenic sources (cf. section 2.1). There are indications of relatively higher Pb concentrations at Site R in relation to the other sites, and relatively higher concentrations of Se at the coastal site. Several of the element concentration values in Fig. 3 (category d) are close to analytical detection limits and/or suffer from relatively high contents and variability in the filters. Whereas the categorisation of these elements into the $< 1 \text{ ng m}^{-3}$ range at all three sites holds (in some cases possibly reaching to around 2 ng m^{-3}) uncertainties thus become too large to enable site-by-site comparisons.

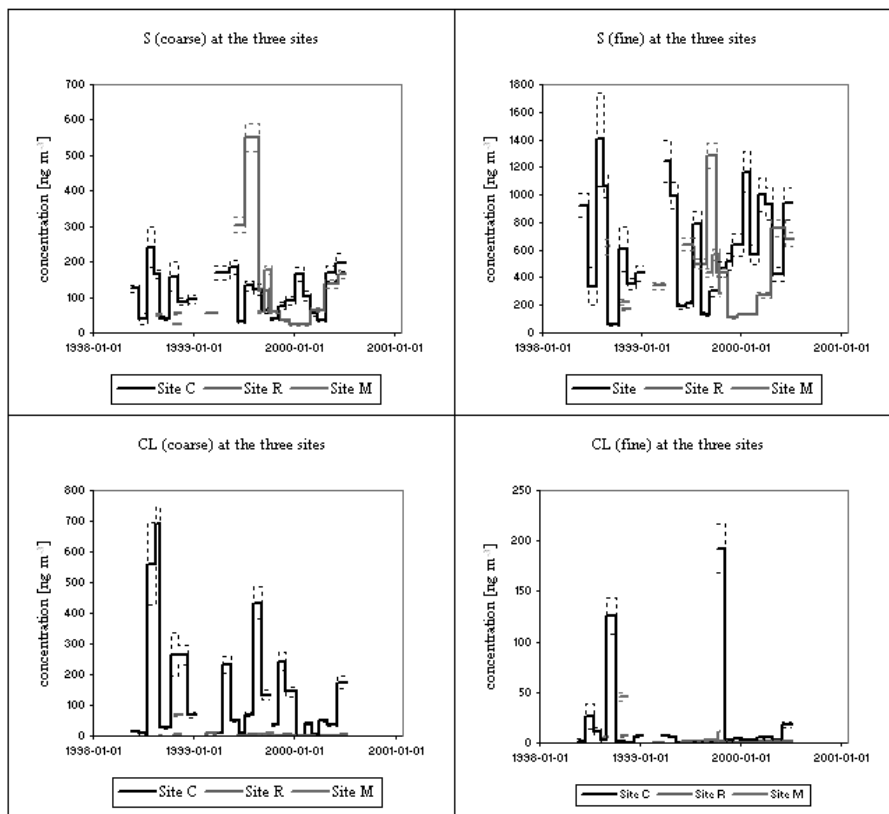


Fig. 2. Time sequence (Sites C, R and M) of coarse-mode (upper, left) and fine-mode (upper, right) concentration levels of sulphur, and of coarse-mode (lower, left) and fine-mode (lower, right) concentration levels of chlorine. Uncertainties at one- σ level indicated by dotted lines.

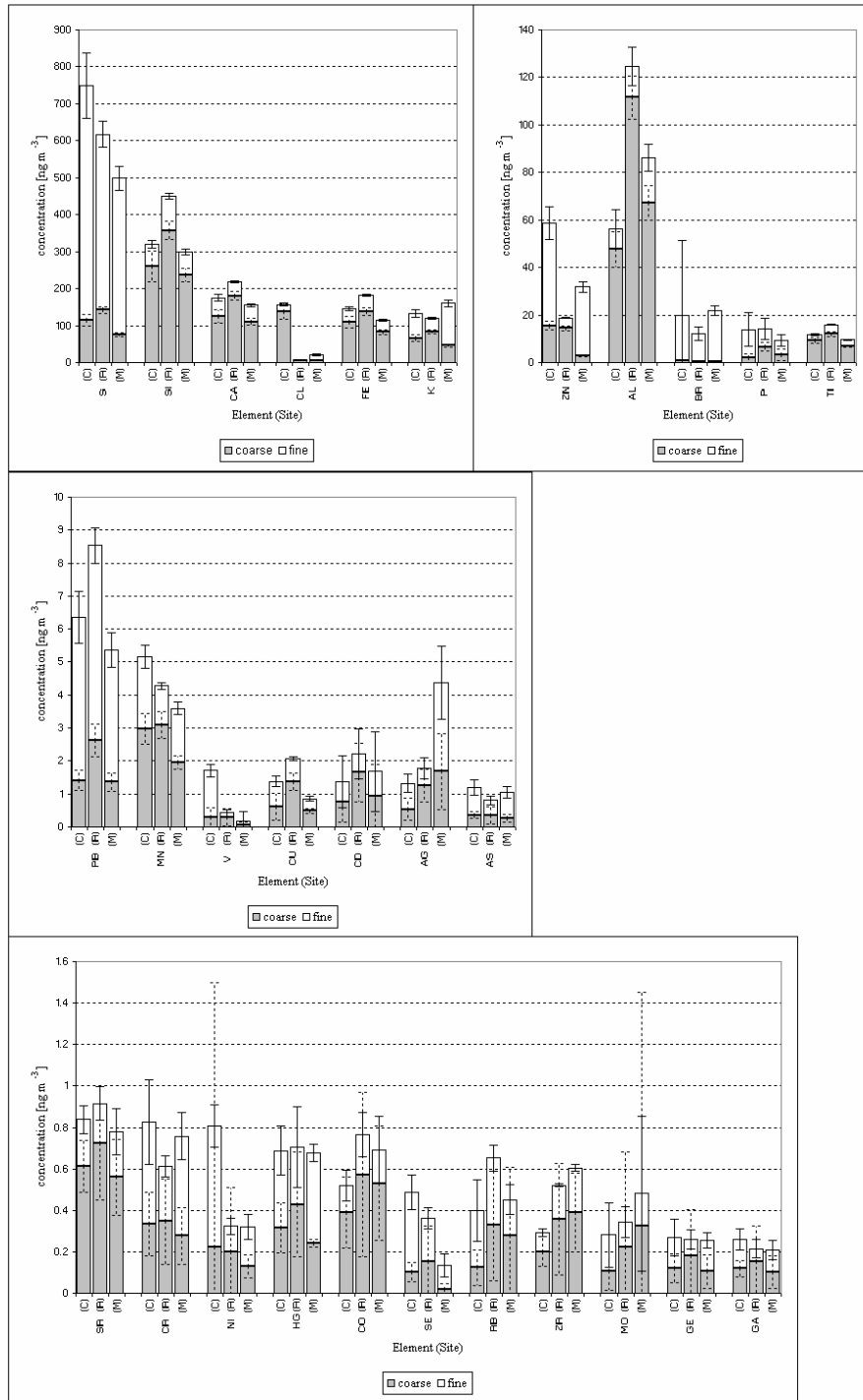


Fig. 3 (previous page). Time-averaged concentration levels (ng m^{-3}), element-by-element and site-by-site, also showing which fraction (coarse or fine) was the main mass-carrier of the element. Error bars (dashed for coarse fractions; smooth for fine fractions) indicate one- σ uncertainties. The graph is organised to show elements as their concentrations decline in the Site-C data set and categorised into four Site-C magnitudes: 100 to 1000 (S, Si, Ca, Cl, Fe, K) (upper, left); 10 to 100 (Zn, Al, Br, P, Ti) (upper, right); 1 to 10 (Pb, Mn, V, Cu, Cd, Ag, As) (middle diagram); and < 1 (Zr, Cr, Ni, Hg, Co, Se, Rb, Zr, Mo, Ge, Ga) (lower). Site-C values based on 24 about 1 month long sampling periods; Site-R values on 11 periods; Site-M values on 5 periods (for elements Co, Ga, Ge, Rb, Sr, Zr, Mo, Hg, Ag time-averaging is based on the last three periods only, since these elements could not be included in the PIXE analysis of filters from the first two periods at Site M).

Coarse- versus fine-fraction tendencies. For Site C, we observe that the elements analysed can be categorised into a clearly coarse-fraction oriented group (Si, Ca, Cl, Fe, Al, Ti, Sr) and a clearly fine-fraction oriented group (S, Zn, P, Pb, V, As, Se). Remaining elements either show indefinite orientation (such as K, Mn) or are associated with uncertainties too large to enable clear categorisation (Br, Cu, Cd, Ag, Cr, Ni, Hg, Co, Rb, Zr, Mo, Ge, Ga). Similar features occur at the mountain sites, but among major differences between the coastal and mountain sites is the fine-fraction dominance at Site M of Cl (probably reflecting a combination of depletion of coarse marine Cl and anthropogenic fine-fraction sources) and K (possibly due to biogenic coniferous-forest sources; cf. Bowen, 1982). Also, Zn is coarse-fraction oriented at Site R (possibly related to coniferous-forest sources; cf., Bowen, 1982; Juniper and Jeffree, 1983).

The above findings can be compared with the results from special measurement efforts (campaigns) in the Ahtopol area (Wiman et al., 2002) during which the aerosol-borne mass of S and Pb was found mainly in the sub- μm particle range. This lends further support to the suggestion that long-distance transports of these elements, both with strong anthropogenic sources (e.g., Schroeder et al., 1987) contributed to the concentrations at Site C. Crustal sources can contribute coarse-fraction Pb (Schroeder et al., 1987) and might underpin the relatively high coarse-fraction concentration level of this element at Site R (cf. Fig. 3c).

In addition to Cl, Ca is an element the mass of which shows particularly clear tendencies towards being carried by coarse aerosol particles. Ca has significant soil and crustal sources contributing to the coarse mode, as has been observed by Lannefors et al. (1983), Wiman and Lannefors (1985), and Allen et al. (2001). Similar considerations apply for Si, Fe, Al, and Ti.

As was the case in the above-mentioned campaigns in the Site C region (Wiman et al., 2002), Mn and Cu show an indefinite tendency, indicating that long-range transports as well as near-regional and local sources contribute to the aerosol composition in this region. These features warrant further investigations, not in the least because deposition-rate calculations of these elements will be strongly dependent on the mass fraction borne by coarse particles.

Concentration levels as briefly compared with other studies. Of major interest would be comparisons with other Black Sea coastal-zone and off-shore aerosol data, but such information is scarce. Compared to data by Hacisalihoglu et al. (1992) and Kubilay et

al. (1995) on aerosol-borne material collected over the Black Sea, our study shows much lower concentrations of Al, Ca, Cr, Mn, Fe and Ni; about the same levels of V, Zn and Cd; and, possibly, higher Co levels. Cl-concentrations in the Eastern Mediterranean atmosphere (Özsoy et al., 2000) are much higher than on the Black Sea coast in our study. Data reported by Pio et al. (1996) for the Southeast European coast (Portugal) give higher values than do our Site-C data, except for Fe and Cd (lower than ours) and Se (on about the same level as in our studies).

Comparisons with Swietlicki et al. (1989) show higher concentrations of S, V and Pb in the Western Baltic than at our coastal site, while concentration levels of Ca, Ti, Fe, and Zn are lower, and those of K, Mn, Ni and Cu are about the same as in our results for the Black Sea coast. In the urban environment outskirts of Budapest (Salma et al., 2002) concentrations of P, Cl, Zn, and As are lower than in our study, and Ti, V, Mn, Cu, Se and Sr are on about the same levels as in our study. Ranges obtained for a coniferous-forest region in south Sweden (Wiman and Lannefors, 1985) are with higher values than those for our Black Sea site, with the exception of those for Fe (and possibly Br), which are close to our data. For most elements, concentrations found at remote locations such as Mauna Loa (Holmes et al., 1997) during non-dust seasons are much lower than those we found during our IEDA measurements. In comparison to our long-term averages for the Black Sea coast, substantially lower concentrations of Cl, K, Ti, V, Mn, Fe, Cu and Zn, but about the same of S and Ni, have been found at Spitsbergen (Heintzenberg et al., 1981).

To the best of our knowledge, no earlier data from the Rhodope and Rila regions exist for comparison with our data set for aerosol-borne concentration levels at our mountain sites. For a general comparison with concentration levels for several trace elements at a well-studied and remote mountain site our data can be related to those obtained by Gatari et al. (2006) at a high-elevation site (3780 m asl) on Mount Kenya (cf. also Gatari et al., 2001). Concentrations found there (fine plus coarse fractions) were for S, Mn, Fe, Ni, Cu, Zn and Pb in the respective ranges (with our Site M to Site R levels for comparison within square brackets), for S: 312-660 [498-617], Mn: 3.6-24 [3.6-4.3], Fe: 130-416 [114-182], Ni: 0.4-1.5 [0.32-0.32], Cu: <0.3-2 [0.86-2.1], Zn: 3.7-12 [32-19], and Pb: 1.5-14 [5.4-8.5] ng m⁻³. This indicates higher Mn-levels, and lower Zn-levels at the Mount Kenya remote site than at our mountain sites, but otherwise suggests concentration levels of the same order of magnitude. Aerosol data from the Alps also exist, but the range of components studied seems mostly focused on particle number concentrations and macro-constituents. For instance, Aymoz et al. (2004) report on aerosol-borne concentrations of Ca²⁺, K⁺, and Cl⁻ in alpine regions before and during a Saharan dust episode. Ca-values ranged from 630 (before dust episode) to 4800 (during episode) ng m⁻³; corresponding values for K and Cl were from 60 to 280 ng m⁻³, and 130 to 900 ng m⁻³, respectively. This can be compared with the concentration levels found at our mountain sites, around 180 ng m⁻³ for Ca, 150 ng m⁻³ for K, and 15 ng m⁻³ for Cl. Average levels for Ca and Cl were thus substantially lower at our Rila and Rhodope sites.

Aerosol-borne element concentration levels at the Bulgarian coastal and montane sites in this study can also be compared with general ranges that are commonly used to indicate whether regions are of remote, rural, or urban (European) type, for a range of elements, notably V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Cd, Hg, and Pb (cf. Schroeder et al., 1987; Seinfeld and Pandis, 1998). Due to the large interval between minimum and

maximum values in the respective categories and the fact that in most cases summarised by Schroeder et al. (1987) values overlap, such indications are fairly rough. However, we observe that for most elements for which there are data for comparative purposes, concentrations found at our sites fall in the categories “remote” and “rural”. In some cases (elements Co, Ni, Cd, and Hg, which might reflect mining and metallurgy enterprises in several parts of Bulgaria; cf. e.g. BMEW, 2001) the concentration levels at our sites are comparable with the ranges provided by Schroeder et al. (1987) for urban European conditions.

Conclusions and implications

Little is known with respect to concentration levels of aerosol-borne compounds in Bulgarian forest regions. In this contribution we have presented results from a month-by-month study, over the period 1998 to 2000, of aerosol-borne concentrations of 29 elements (Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ge, As, Se, Br, Rb, Sr, Zr, Mo, Cd, Hg, Ag, and Pb) at a coastal site over the period 1998 to 2000, and also month-by-month data, albeit covering more limited periods, from high-elevation mountain sites in Bulgaria. Although our data sets contain some gaps our findings are in several respects new for the regions involved (the southern Bulgarian Black Sea, and the Rhodope and Rila mountain ranges).

We have exemplified temporal concentration variations at the sites through showing the highly variable patterns exhibited by coarse- and fine-fractions of S and Cl. Among features with respect to the average (time-weighted) total (coarse plus fine fractions) concentration levels of elements, the coastal-site data set showed elements S, Si, Ca, Cl, Fe, and K residing in the concentration (ng m^{-3}) range 100 to 1000; Zn, Al, Br, P, and Ti in the 10 to 100 range; Pb, Mn, V, Cu, Cd, Ag, and As in the 1 to 10 range; and Zr, Cr, Ni, Hg, Co, Se, Rb, Zr, Mo, Ge, and Ga below 1. The average Cl concentration at the coastal site was up to a factor 20 higher than at the mountain sites. Also, the S, V, Zn and Se concentrations were higher at the coastal site (V being in the $<1 \text{ ng m}^{-3}$ range at the mountain sites) which likely indicates a combination of marine and anthropogenic sources. The average concentration of Al was higher at the mountain sites. There were indications of relatively higher Pb concentrations at the Rhodope mountain site in relation to the other sites. Several of the concentration values for elements Zr, Cr, Ni, Hg, Co, Se, Rb, Zr, Mo, Ge, and Ga were close to analytical detection limits and/or suffer from relatively high contents and variability in the filters. These elements can be categorised into the $< 1 \text{ ng m}^{-3}$ range at all three sites.

At the coastal site, elements Si, Ca, Cl, Fe, Al, Ti, and Sr were clearly coarse-fraction oriented, and S, Zn, P, Pb, V, As, and Se clearly fine-fraction oriented. Remaining elements either showed indefinite orientation (such as K, Mn) or were associated with uncertainties too large to enable clear categorisation. Similar features occur at the mountain sites, but among major differences were that Cl and K at the Rila site were fine-fraction dominated and that Zn at the Rhodope site was coarse-fraction oriented.

Aerosol-borne element concentration levels at the Bulgarian coastal site in this study are compared with results from a few off-shore studies relating to the Black Sea. The

comparison suggests much lower concentrations of Al, Ca, Cr, Mn, Fe and Ni at our Bulgarian coastal site, whilst levels of V, Zn, and Cd are similar. Comparisons with other marine environments (the Mediterranean; Southeast European coast; Western Baltic) are also made. We have not found any data from Bulgarian montane environments for relevant comparisons. However, comparing our data with those published from a study at a remote mountain site (Mount Kenya) suggests, with a few exceptions (Zn, Mn) fairly similar concentration levels. Comparisons with macro-constituent (Ca, Cl) data from the Alps indicate that concentration levels at the Bulgarian mountain sites studied here were lower.

Our data sets from the three sites are also compared with general levels commonly used to indicate whether regions are of remote, rural, or urban type. Although such indications are fairly rough we observe that for most elements for which there are data for comparative purposes, levels found at our sites fall in the categories "remote" and "rural". In some cases (elements Co, Ni, Cd, Hg) the concentration levels at our sites might be comparable with urban European conditions.

The study reported on above should be seen in the broader context of several research questions of importance to understanding the Bulgarian coastal-zone and montane-forest biogeochemistry, and to assessing forest vitality, not in the least with respect to the interlinked biogeochemistry-and-climate-change framework (Wiman et al., 1990; Karnosky et al., 2003; IPCC, 2007). Some possibilities for source and source-region identifications are inherent in our aerosol data set. It also holds opportunities for being used as input to deposition models, for instance of the kind developed by Wiman and Ågren (1985).

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Трасерни елементи в аерозола в България: нива на концентрация в брегови и планински райони

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Резюме: Не се знае много за ултрамикроелементните концентрации в България. Тук се предлагат резултатите от изследване за концентрациите на Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ge, As, Se, Br, Rb, Sr, Zr, Mo, Cd, Hg, Ag и Pb в аерозолите в южната част на Българската крайбрежна зона на Черно море, централните Родопи и западната част на Рила. Нашите изследвания са относително нови за тези райони. Средните по време концентрации (ng m^{-3}) в бреговата зона за S, Si, Ca, Cl, Fe, и K са в интервала от 100 до 1000; за

Zn, Al, Br, P и Ti от 10 до 100; за Pb, Mn, V, Cu, Cd, Ag и от 1 до 10; докато Zr, Cr, Ni, Hg, Co, Se, Rb, Zr, Mo, Ge и Ga са под 1. Нивата на S, Cl, V, Zn и Se са по-високи в крайбрежната зона (Cl около 20 пъти повече). Si, Ca, Cl, Fe, Al, Ti и Sr доминират при по-големите частици, докато S, Zn, P, Pb, V, As и Se доминират при по-финната фракция на аерозолите в крайбрежната зона. Подобно поведение е характерно и за планинските райони, но Cl и K в Рила доминират при по-големите частици, а Zn в Родопите доминира при по-финните аерозоли. Нивата установени на нашите полигони попадат в класификацията на “отдалечени” или “извънградски” концентрации, но в някои случаи (Co, Ni, Cd, Hg) те могат да се възприемат като “градски”. Нашите изследвания дават възможност за идентификация на областите на произход и имат принос към моделите на атмосферното отлагане на посочените замърсители на въздуха. Необходими са повече изследвания за оценка на тези и други сериозни проблеми свързани с качеството на въздуха и състоянието на горите в България.