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ESTIMATIONS OF TOTAL CARBON (TC) AND SEVERAL METALS IN THE COMPOSITION OF PARTICULATE MATTER IN BUCHAREST AREA*

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Abstract. Ambient suspended Particulate Matter (PM_{10}, TSP) were collected from July 2008 to October 2008, in urban and rural sites of Bucharest area. The metallic species (Cd, Pb, Mn and Ni) and total carbon (TC) content were analyzed. Ni and TC were found in higher concentrations in urban site.

Key words: total carbon, PM_{10}, TSP, lead, nickel cadmium, manganese.

1. INTRODUCTION

Atmospheric particles have an important role on climate by radiative forcing and by altering cloud properties, precipitation efficiency and ice formation [1,2] but are also responsible of a several human health effects like: respiratory, cardiovascular, allergic and lung cancer diseases [3–5]. All these characteristics of airborne particulate matter depend on their concentration, size and chemical composition [1, 6, 7].

Likewise, Pb, Cd, Mn, and Ni anthropogenic emissions are more important than natural sources such as continental dust, volcanic dust and gas, sea spray, and biogenic particles. The main anthropogenic sources of heavy metals are industrial sources especially mining activities, foundries, and smelters and diffuse sources such as piping, constituents of products, combustion by-products and traffic [8].

EC/BC (elemental carbon knew also as black carbon) is emitted directly in particulate form during incomplete combustion of carbonaceous fuels. These

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particles contain also OC (organic carbon) with proportions depending on fuel and combustion characteristics (*e.g.* fresh diesel soot contains 76% BC; [9]). Particulate OC can be emitted directly or formed through photochemical reactions from gaseous precursors [10]. Determination of TC (total carbon) – sum between BC/EC and OC – contribute on estimate the carbonaceous compounds contained in particulate matter.

Research studies dedicated to air quality in Romania, were mainly focused on atmospheric gaseous compounds [11–13]. The present ambient air quality study was focused on ambient suspended particulate matter being undertaken in urban and rural sites on Bucharest area from July 2008 to October 2008. At both monitoring sites, ambient level of PM_{10} and TSP were measured using a gravimetric system. The sites and methods are described in Section 2. In Section 3 are presented the results related to both the PM mass concentration and total carbon composition. Because the heavy metals identified in the environmental samples are toxic for living organisms even at low concentration [14–17], the mass concentration of Pb, Mn, Cd and Ni associated to PM_{10} and TSP were evaluated.

2. SAMPLING SITES AND METHODOLOGY

There were selected two sampling sites which are representative for urban and rural sites. Urban site (noted US) is located in centre of Bucharest (relatively at 500 m from "zero kilometre" site) having the following coordinates: $44^0$26'17" North, $26^0$06'19" East, at 93 m a.s.l. This site sampling is surrounded on all directions by high buildings corresponding and is influenced mainly by road traffic emissions. The sampling point for rural site (noted RS), with $44^0$40'42" North, $26^0$15'50" East, at 81 m a.s.l. is surrounded by farming land and a small forest situated at approximately 35 km from Bucharest. In urban site, there were collected PM_{10} and TSP particles and in rural site were collected only PM_{10} particles but all samples were collected at a height around of 10 m corresponding for regional studies [18].

Each 10 PM_{10} and TSP samples were collected in every month corresponding for the period: July 2008–October 2008 only on weekdays. Each sample was collected for a 24 hour period on glass fibre filter (Whatman, Schleicher&Schuell, 47 mm diameter) using 2 medium-volume air samplers for PM_{10} (Sven Leckel, Germany) and one for TSP (Aquanta) for urban site. The average flow rate used in urban site for PM_{10} sampling was 2.3 m^3/h min and 1.8 m^3/h for TSP; in rural site, the flow rate was set on 3.2 m^3/h for PM_{10} sampling. For filters weighing was used an analytical balance (with 0.00001g precision). Filters were kept in open Petri dishes in desiccators in weighing room at a constant temperature of 20±1°C, relative humidity 50± 5% for having a constant mass of them before and after sampling.

For Pb, Ni, Mn and Cd analysis, samples were mineralized using a microwave oven Milestone Digestor Ethos Sel on a 20 minutes program using 6 mL HCl, 2 mL HNO_3 and 1.5 mL HF for a complete digestion and the Pb, Ni, Mn and Cd elements were determined using a graphite furnace atomic absorption spectrometer (GF-AAS) Thermo Solaar M5. Blanks were also prepared in the same conditions.

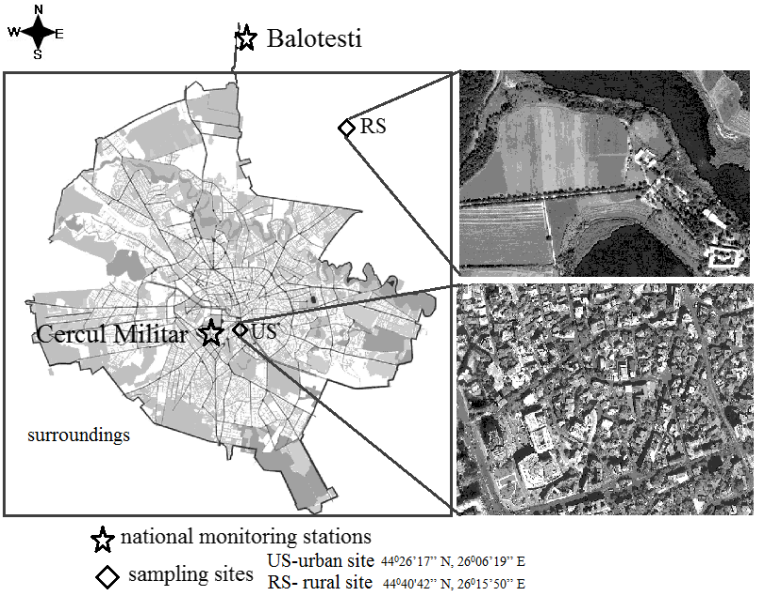


Fig. 1 – Representation of sampling sites.

A total carbon (TC) analyzer (Thermo Scientific) provided with a device for solids samples was used to estimate the TC associated to PM_{10} and TSP particles. Total carbon (TC) is defined as the sum of the elemental carbon (EC), organic carbon (OC) and carbonate carbon (CC) in an aerosol sample and thermal analysis is one of the most widely used for the determination of the mass of TC concentrations [19, 20].

3. RESULTS AND DISCUSSIONS

3.1. MASS CONCENTRATION

In this section, time series of PM_{10} and TSP concentrations are explored with respect common temporal patterns in rural and urban stations. The corresponding mean concentration for *summer season* (July- September 2008) was 17.61 $\mu g/m^3$ in urban site but PM_{10} concentrations varied on a large domain (15.04–71.93 $\mu g/m^3$)

(Fig. 2a). In rural site were observed lower concentrations than in urban site (10.53–46.44 μg/m^3).

The daily variation of particulate matter concentrations has been examined. The analysis did not reveal any characteristic weekly pattern common for the two stations (Fig. 2b). The arithmetic average of daily concentrations during weekdays in rural site was 26.30 μg/m^3 varying in a narrow domain (10.53–46.44 μg/m^3). This suggested that no extreme regional pollution episode was registered during sampling period. Instead, in urban site, it was observed that in Mondays and Fridays (first and last weekdays) were registered the highest concentrations probably due to the increased traffic density [21]. In our following studies will try to verify if this pattern depending on weekdays will remain. The arithmetic average of daily concentrations in urban site was 40 μg/m^3 but their variation took place on a large domain (15.04–71.93 μg/m^3) likely due to the anthropogenic sources agglomeration.

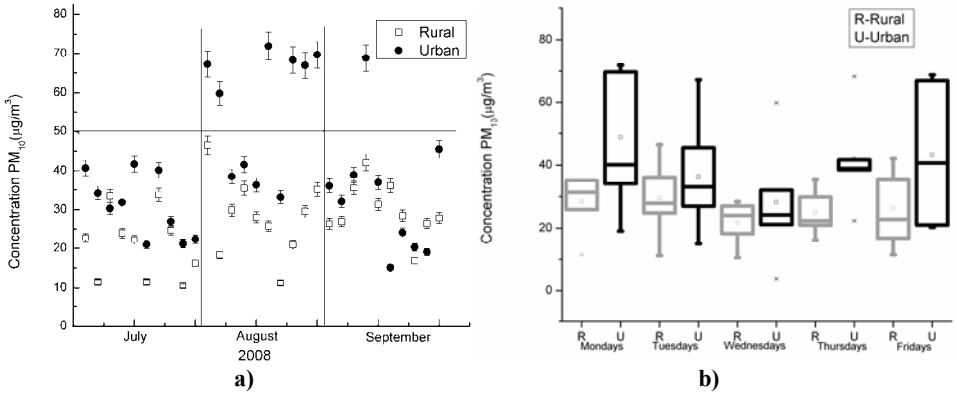
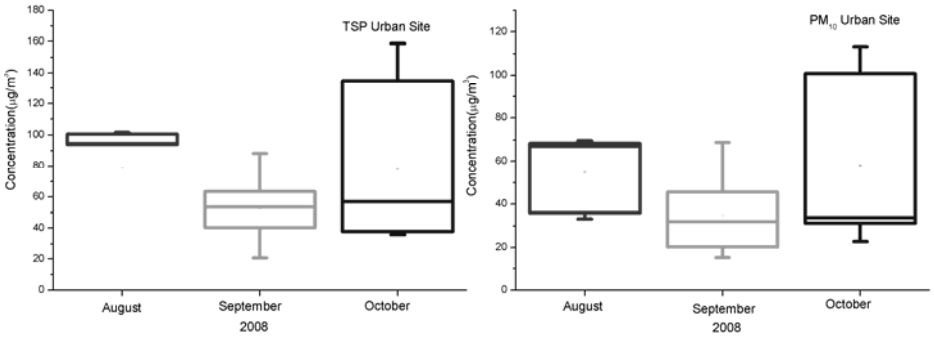


Fig. 2 – a) Temporal variation of PM10 mass concentrations in urban and rural sites; bar errors are also presented; b) week variation of PM10 mass concentrations in urban and rural sites.

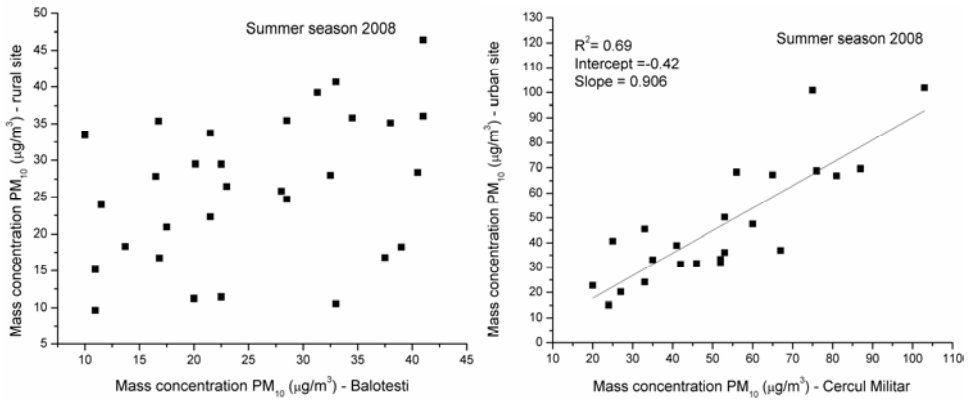
PM_{10} and TSP concentrations for August-October 2008 period in urban site were distributed as shown in Fig. 3, having similar trends. Since regulations rely upon arithmetic averages, our discussion focuses on arithmetic average concentrations. The average PM_{10} concentrations during the months August, September and October for urban site, were: 54.81 μg/m^3, 34.81 μg/m^3 and 57.97 μg/m^3 respectively. Thus, it can be observed that PM_{10} average concentrations were higher than the European Union air quality annual PM_{10} standard of 50 μg/m^3 [18] in August and October 2008. In case of TSP, the average concentrations during the months August, September and October for urban site, were: 93.86 μg/m^3, 52.72 μg/m^3 and 78.02 μg/m^3 respectively being lower than the national threshold of 150 μg/m^3. The lower values of PM_{10} and TSP mean concentrations registered for September can be explained by increasing of pollutants dispersion due to enhanced air circulations.



a) **b)**

Fig. 3 – Urban site: a) TSP concentration; b) PM_{10} concentration for August–October period.

The measured PM_{10} concentrations were compared with the data from monitoring stations of Bucharest Environment Agency closed to urban (Cercul Militar) and rural (Balotesti) stations. In case of rural site comparison, the measurements are largely uncorrelated [22]. The values of regression line slope = 0.38147, intercept = 16.53953 and linear correlation coefficient, R^2 = 0.11993 for a number of data points, N=30 suggested high differences of particulate matter sources both natural and anthropogenic.



a) **b)**

Fig. 4 – Comparison between PM10 concentrations: a) rural site-Balotesti; b) urban site – Cercul Militar.

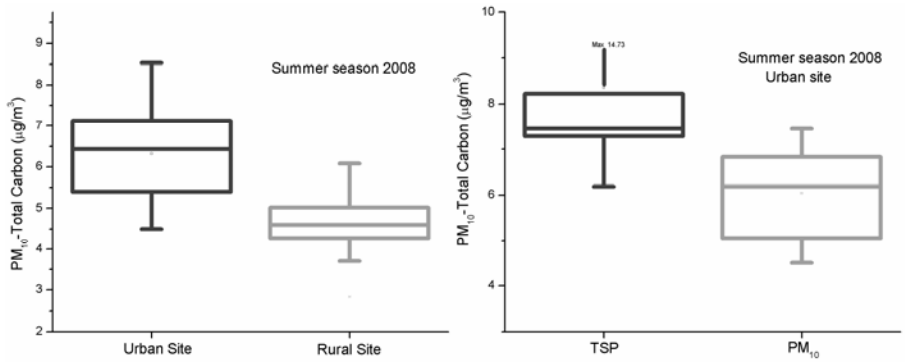
Regression line slope, intercept, and R^2 are given in Fig. 4b for urban site comparison. The number of data points (N) was reduced in urban site from 30 to 24 because there was found no data for urban station-Cercul Militar for 6 days. The value of intercept near to 0 suggested that sources are probably similar in the both urban sites (mainly traffic), and value of R^2 show a relatively good agreement

between the two urban sites taking into account that possible other local sources may strongly influence PM10 mass concentration [23].

3.2. VARIATION OF TOTAL CARBON CONTENT

The environmental relevance of the carbonaceous aerosol comprises a number of important topics, such as human health, direct and indirect climate forcing, and air-quality. The high number of organic molecules reported to be associated with ambient fine aerosols have a wide range of different physical and chemical properties, of which impact on human health and cloud formation largely remains unknown. Furthermore, black carbon is the principal light absorbing species in the atmosphere, significantly affecting the Earth's radiative balance [24]. We analyzed the total carbon (TC) in aerosol particles.

The highest TC content associated to PM_{10} particles was found in urban site, in the summer season (8.53 μg/m^3) and the lowest TC content was found in rural site in winter season (0.007 μg/m^3) (data not published yet). The lower concentrations in winter season were explained due to the high values of relative humidity that intensify the removal processes of particles from the atmosphere. Compared with data from wintertime can be observed that TC content registered generally low values but few maxima large the domain. In summer season, values of TC content varied on a median value of 6.31 μg/m^3 in urban site and 4.57 μg/m^3 in rural site.



(a) **(b)**

Fig. 5 – (a) Variation of TC content associated to PM_{10} fraction in urban and rural sites in summer season; b) comparison between TC content on TSP and PM_{10} for urban site in summer season.

Additionally, TC content in PM_{10} and TSP was 1.9 higher in urban samples than in rural samples. TC content for TSP particles registered a small shift until 14.73 μg/m^3 (Fig. 5b). Although, if TC content is correlated only with the particle mass (μg) deposited on filter, it can be observed that total carbon content represent

a higher percent from mass of particles in the winter (data not published yet). As conclusion high TC concentrations were associated to PM_{10} particles than to TSP.

3.3. VARIATION OF Cd, Pb, Ni AND Mn CONTENTS ASSOCIATED TO PM_{10} AND TSP

The Cd concentrations values, with 1 or 2 orders of magnitude lower in comparison with the other metals (Pb, Ni, Cd) may be the result in some part due to it slow volatility and to emission at high temperature that are very limited [25] (Fig. 6).

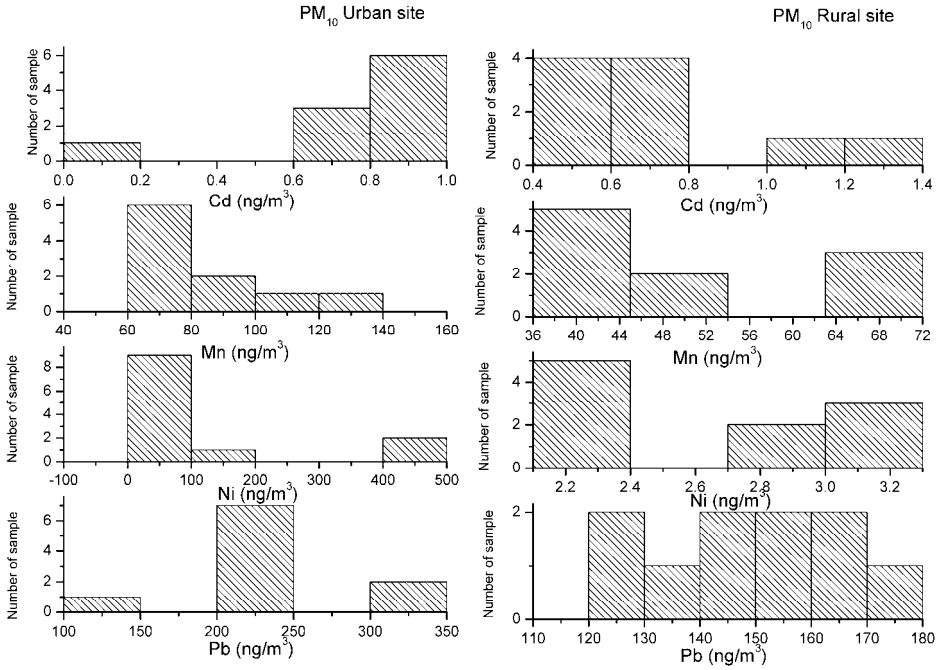


Fig. 6 – Variation of Pb, Ni, Mn and Cd associated to PM_{10} during summer season in urban and rural sites.

Kim *et al.* (2007) made correlation analysis of Cd content from 13 stations in Korea for a 14 years period. Their results suggested that Cd concentrations from a station are apt to share strong homogeneity with the other stations from surrounding areas [26]. This may explain the closeness between the Cd concentrations in urban site (0.76 ng/m^3) with those from rural site (1 ng/m^3) emphasized by the high transferability of Cd between different environmental reservoirs [26]. As may be seen, Cd concentration associated to PM_{10} was lower than the European Union threshold 5 ng/m^3 [27].

Nriagu *et al.* (1986) found that anthropogenic sources contribute with more than 90% at the global Cd emissions [28]. Studies of ice core samples indicated that Cd levels may have reached a maximum in the 1960 and then a decrease was registered constantly until 1994 [29]. Until now, many studies have confirmed that Cd emissions decreased both on local and on global scales [30]. Our data are insufficient to draw a pattern for showing a concentrations tendency through time but revealed that these concentrations in Bucharest area are similar to those found in other studies [31] and in other European cities, even smaller in some cases [32].

Lower concentration but close values of Pb were registered in rural site, due in part to homogeneity of Pb distribution (150 ng/m^3). In urban site, values of Pb concentration varied on a very large domain (100–350 ng/m^3) and it is expected that the Pb distribution to be affected more sensitively by anthropogenic source processes (*e.g.* under the heavy traffic conditions) [33]. In addition, many studies focused on Pb associated to PM_{10} explain the spatial and time distribution through the combined effects of source/ sink processes and meteorological conditions [34]. Mn concentrations are very scattered not only in urban but also in rural site because until now there are no regulations to impose thresholds for this pollutant. One reason that raises the complexity grade in evaluating the correct value of Mn concentration threshold is the fact that manganese is an element frequently found in soil composition [35]. Also it can be observed that mean Mn concentration in rural site, 47.39 ng/m^3, is about 1.72 lower from mean concentration from urban site, 81.68 ng/m^3 (Fig. 6).

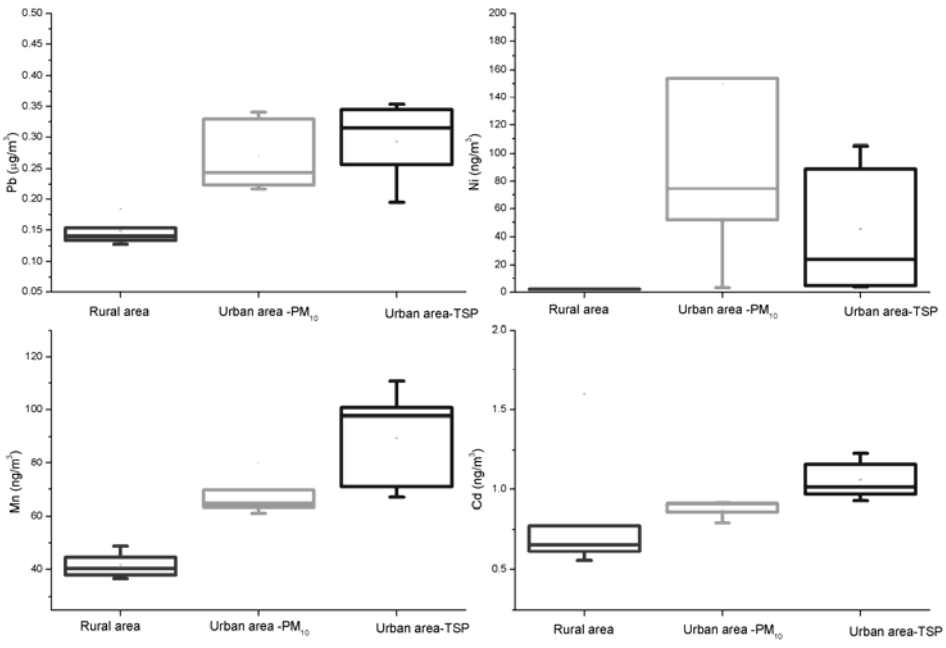


Fig. 7 – Variation of Pb, Ni, Mn and Cd associated to PM_{10} and TSP during summer season.

Ni concentrations in PM_{10} samples were very different from rural (2.61 ng/m^3) to urban site (126.13 ng/m^3). This may reflect the anthropogenic origin of Ni in PM_{10} content, in urban site. Nowadays, Directive 2004/107/EC implies that Ni concentration to be 20 ng/m^3 for the total content in the PM_{10} fraction averaged over a calendar year [27]. In conclusion, it is necessary to implement a daily Ni concentration monitoring plan in Bucharest at least.

Such as expected, the lower contents in metals (Pb, Ni, Mn, Cd) were found in PM_{10} sampled in rural site (Fig. 7) Pb and Ni presents lower concentrations in TSP, indicating that these metals have affinity to PM_{10} than TSP. Mn and Cd showed similar trends being in relatively higher concentrations in TSP deposits but if Mn and Cd is related to particles mass from the filter, it will be observed that are no affinity to a specific fraction (PM_{10} or TSP).

4. CONCLUSIONS

Ambient concentrations of PM_{10} in rural site showed that no extreme pollution episode took place on during sampling campaign. In urban site it was identified a possible pattern which revealed that in weekdays the highest concentrations are in Mondays and Fridays. Our following studies will verify and argument the existence of this pattern or other pattern. The comparison of our measured concentrations with data from monitoring stations of Bucharest Environment Agency stations (Cercul Militar - urban site, Balotesti - rural site) emphasized that only in urban site, the sources are the same and it was found a good correlation between sites. In case of rural site, no correlation was found primary due to different sources.

TC content was higher in urban PM_{10} samples showing that TC is found preferentially in PM_{10} samples.

The concentration of Cd, Pb, Mn, and Ni associated to PM_{10} samples were discussed and the following conclusions were drawn:

– Cd concentrations were lowest and not pass the EU threshold;

– low concentrations of Pb were registered in rural site and in urban site, Pb distribution is affected more sensitively by anthropogenic source processes;

– Mn concentrations are very scattered not only in urban but also in rural site because until now there are no regulations to impose thresholds;

– the high Ni concentrations in PM_{10} samples justify the necessity to implement a daily Ni concentration monitoring plan in Bucharest.

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REFERENCES

1. Houghton, J.T., Y. Ding, D.J. Griggs, M. Noguer, P.J. van der Linden, X. Dai, K. Maskell, and C.A. Johnson, *Climate Change*: *The Scientific Basis. Contribution of Working Group I to the Third Assessment Report of the Intergovernmental Panel on Climate Change,* IPCC, 2001Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA, 2001.
2. U. Lohmann, J. Feichter, *Global indirect aerosol effects: A review*, Atmos. Chem. and Phys., **5**, 715–737 (2005).
3. N. Künzli, R. Kaiser, S. Medina, *Public-health impact of outdoor and traffic-related air pollution: a European assessment*, Lancet*,* **356**, 795–801 (2000).
4. L.J. Donaldson, R. J, Donaldson, *Essential public health*, Second Edition, Radcliffe Publishing United Kingdom, 2003.
5. J.A. Bernstein, N. Alexis, C. Barnes, I.L. Bernstein, A. Nel, D. Peden, D. Diaz-Sanchez, S.M. Tarlo, P.B. Williams, *Health effects of air pollution*, Journal of Allergy and Clinical Immunology, **114**, 1116–1123 (2004).
6. Y.J. Kaufman, D. Tanre and O. Boucher, *A satellite view of aerosols in the climate system*, Nature, **419**, 215–223 (2002).
7. C.G. Popescu, *Relation between vehicle traffic and heavy metals content from the particulate matters*, Romanian Reports in Physics, **63**, *2*, 471–482 (2011).
8. S.L. Gong and L.A. Barrie, *Trends of heavy metal components in the arctic aerosols and their relationship to the emissions in the Northern Hemisphere*, STOTEN, **1–3**, 175–183 (2005).
9. T.C. Bond, D.G. Streets, K.F. Yarber, S.M. Nelson, J.-H. Woo, Z. Klimont, *A technology-based global inventory of black and organic carbon emissions from combustion*, J. Geophys. Res., **109** (2004).
10. M.Z. Jacobson, *A physically-based treatment of elemental carbon optics: implications for global direct forcing of aerosols*, Geophys. Res. Lett., **27**, *2*, 217–220 (2000),
11. F. Popescu, I. Ionel, N. Lontis, L. Calin, I.L. Dungan, *Air quality monitoring in an urban agglomeration*, Rom. Journ. Phys., **56**, *3–4*, 495–506 (2011).
12. V. Cuculeanu, R. Sterrer, G. Mocioaca, G. Schimak, M. Anghel, *Design of the air quality monitoring network for Bucharest city,* Romanian Reports in Physics, **62**, *2*, 383–395 (2010).
13. G. Rusu-Zagar, L. Filip, S. Stefan, R. Stepa, *Model for control of indoor air quality in an industrial environment*, Romanian Reports in Physics, **63**, *1*, 196–207 (2011).
14. G. State, I. V. Popescu, A. Gheboianu, C. Radulescu, I. Dulama, I. Bancuta, R. Stirbescu*, Identification of air pollution elements in lichens used as bioindicators by the XRF and AAS methods*, Rom. Journ. Phys., **56**, *1–2*, 240–249 (2011).
15. C. Stihi, C. Radulescu, G. Busuioc, I.V. Popescu, A. Gheboianu, A. Ene, *Studies on accumulation of heavy metals from substrate to edible wild mushrooms*, Rom. Journ. Phys., **56**, *1–2*, 257–264 (2011).
16. I. V. Popescu, M. Frontasyeva, C. Stihi, GH. V. Cimpoca, C. Radulescu, A. Gheboianu, C. Oros, GH. Vlaicu, M. Petre, I. Bancuta, I. Dulama, *Nuclear and nuclear related analytical methods applied in environmental research*, Rom. Journ. Phys., **55**, *7–8*, 821–829 (2010).
17. A. Ene, I. V. Popescu, C. Stihi, A. Gheboianu, A. Pantelică, C. Petre, *PIXE analysis of multielemental samples*, Rom. Journ. Phys., **55**, *7–8*, 806–814 (2010).
18. *** Council Directive 1999/30/EC *relating to limit values for sulphur dioxide, nitrogen dioxide and oxides of nitrogen, particulate matter, and lead in ambient*, OJ L 163, 29, 41–60 (1999).
19. H. Puxbaum, *Application of two thermo-gas analyzers for atmospheric aerosol characterization*, J. Environ. Anal. Chem. **10**, 1–16 (1981).
20. B. J. Turpin, P. Saxena, E. Andrews, *Measuring and simulating particulate organics in the atmosphere: problems and prospects*, Atmos.Environ., **34**, 2983–3013 (2000).
21. G. Buzorius, K. Hämeri, J. Pekkanen, M. Kulmala, *Spatial variation of aerosol number concentration in Helsinki city*, Atmos.Environ., **33**, 553–565 (1999).

22. G.P. Ayers, *Comment on regression analysis of air quality data*, Atmos. Environ., **35**, 2423–2425 (2001).
23. S. Kinghama, M. Duranda, T. Aberkaneb, J. Harrisona, J.G. Wilsona, M. Epton, *Winter comparison of TEOM, MiniVol and DustTrak PM10 monitors in a woodsmoke environment*, Atmos. Environ., **40**, 338–347 (2006).
24. J.E.Penner, C.C. Chuang, K. Grant, *Climate forcing by carbonaceous and sulfate aerosols*, Clim. Dyn. **14**, 839−851 (1998).
25. M.A.Yatsenko-Hmelevskaya, V.V.Tsibulsky, B.V. Milyaev, *Migration of heavy metals in the atmosphere*, Journal of Ecological Chemistry, **3**, *1*, 3–15, (1994)
26. K.-H. Kim, *Airborne cadmium in the major monitoring locations in Korea between 1991 and 2004,* Atmos. Environ., **41**, 4380–4395 (2007).
27. *** Council Directive 2004/107/EC *relating to arsenic, cadmium, mercury, nickel and polycyclic aromatic hydrocarbons in ambient air*, Off. J. of European Council, 2004.
28. J.O Nriagu, *Cadmium in the atmosphere and in precipitation*, Cadmium in the Environment, Wiley, New York, 71–114, 1986.
29. C.F. Boutron, J.P.Candelone, S.M. Hong, *Past and recent changes in the large-scale tropospheric cycles of lead and other heavy metals as documented in Antarctic and Greenland snow and ice—a review*, Geochimica et Cosmochimica Acta, **58**, *15*, 3217–3225 (1994).
30. J.M. Pacyna, E.G.Pacyna, *An assessment of global and regional emissions of trace metals to the atmosphere from anthropogenic sources worldwide,* Environmental Reviews, **9**, 269–298 (2001).
31. S. Stefan, C. Raicu, *The analyses of the air pollution episodes in Bucharest,* Proceedings of National Physics Conference, 2008.
32. E. G. Pacyna, J.M. Pacyna, J.Fudala, E.Strzelecka-Jastrzab, S. Hlawiczka, D. Panasiuk, S. Nitter, T. Pregger, H. Pfeiffer, R. Friedrich, *Current and future emissions of selected heavy metals to the atmosphere from anthropogenic sources in Europe*, Atmos. Environ., **41**, 8557–8566 (2007).
33. G.C. Fang, C.N. Chang, Y.S. Wu, P.P.C. Fu, C.J. Yang, C.D. Chen, S.C. Chang, *Ambient suspended particulate matters and related chemical species study in central Taiwan, Taichung during 1998–2001*, Atmos. Environ., **36**, 1921–1928 (2002).
34. V.K. Mishra, K.-H. Kim, C.-H. Kang , K.C. Choi, *Wintertime sources and spatial distribution of airborne lead in Korea*, Atmos. Environ., **38**, *17*, 2653–2664 (2004).
35. L. Lacatusu, N. Anastasiu, M. Popescu, P. Enciu, *Geo-Atlas of Bucharest municipality* (in Romanian), EstFalia Publishing House, 2008.