

# Studying Atmospheric Dust and Heavy Metals on Urban Sites through Synchronous Use of Different Methods

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**Abstract** Outdoor dust as a pollutant is also a transit environment for different pollutants emphasizing heavy metals. Commonly, it is urban population, who is exposed to the maximal adverse impact of dust and associated pollutants. In most cases, urban atmosphere researches are implemented on a few permanent monitoring stations. Data obtained from these stations cannot be sufficient enough to provide a real picture of atmospheric pollution. The most detailed information is obtained from synchronous instrumental sampling (aspiration) and studies of indicator environments (snow cover, leaves). This research pursued assessment of levels of dust and heavy metal pollution of near-surface air through different methods on the example of city of Yerevan (Armenia). The city area comprises a complex mosaic of natural and man-made sources of dust and heavy metals. So, for many years Yerevan has been exposed to high dust and associated heavy metals pollution levels. The research was implemented in 2011 through 2012 and included spatially coherent snow and tree leaf sampling, and instrumental sampling of dust and allowed assessing dust and heavy metal load and contents on the entire territory of Yerevan, identifying pollution sources, contouring ecologically unfavorable sites and finally identifying risk groups among the population.

**Keywords:** *urban air pollution, dust, heavy metals, alternative research methods*

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## 1. Introduction

It is known that outdoor dust is not only an environmental pollutant, but also a transit medium for different environmental pollutants and heavy metals (HM) in particular [16]. Today, it is urban population, who is most exposed to adverse impacts of dust and dust-associated pollutants [15] as a modern city combines a variety of economic activities with numerous pollution sources and high density of population [4].

Commonly, dust and HM pollution researches on urban sites are implemented on a few permanent monitoring stations [3]. Automated air sampling methods are used widely, however they have a number of limitations such as expensive equipment, labour-intensive and expensive maintenance and service, and so on. So, it is obvious that the number of such stations is too limited. This makes the setting up of a regular sampling grid unrealistic.

Such disadvantages may be compensated by alternative research methods with application of indicator mediums. The latter allows setting up a regular grid of sampling throughout urban areas, whereas localization of sampling sites may vary depending on research tasks so as to assure representativeness of data obtained. One of major result of this indicator medium research is the generated set of complementary informative air pollution parameters [4,9,14], the analysis of which allows assessing both dust

and HM load, contour ecologically unfavorable sites throughout a city, identify risk groups among the population, assess health risks [2,10] and finally develop appropriate risk reduction measures.

This research was aimed at assessment of near-surface air pollution levels with dust and HM through different methods on the example of city of Yerevan (Armenia).

Yerevan – Armenia's capital city – covers an area of 227sq.km. It is situated in north-east of Ararat valley in the canyon of River Hrazdan. The relief is sufficiently diverse and is shaped as plains, plateaus, foothills, canyons.

The climate is continental with rather broad temperature daily and seasonal amplitude. Summers are hot, dry and long-lasting, winters are cold and short. Mean annual temperature varies from +8.80 to +11.60, with summer mean +22°C, winter mean –20°C, snow cover is not common for every year: The temperature regime of the city is strongly impacted by slope aspect and large altitudinal variations (850-1420 m a.s.l.). Mean air temperature of the lower central and upper suburban parts of the city varies 1.5 to 2.0°C. The annual norm of precipitation varies from 300 to 350 mm. Main precipitations occur in the spring and autumn.

The natural landscape of the city area is mainly semi-desert (predominant) and arid steppe.

The geological structure of the area is dominated by volcanic lavas, tuffs and Quaternary sediments characterized by close-to-Clarke contents of HM ( $Zn_{(9,4)}$ –

$\text{Cu}_{(2,9)}\text{-Co}_{(1,8)}$ ). The soil is mostly of brown semi-desert type, soil profile is rich in carbonates and the lower horizon presence of gypsum is common, this providing a favorable environment for HM accumulation on soil profiles [11].

For years Yerevan was distinguished by high levels of dust pollution of atmospheric air and intense geochemical anomalies of HM in transit and depositing mediums [12,13]. The city houses the major part of Armenia's industrial enterprises (42%) and population (34%); heavy traffic loads, too, are common to Yerevan. Major industrial branches are food production, jewelry, chemical and metalworking industries. Most of industrial enterprises are located in the south, in the so-called industrial part of the city. Another peculiarity of Yerevan is that it comprises 39 active deposits and mines of tuff and basalt, sand and gypsum which add to the dust load on the city.

## 2. Materials and Methods

This dust research was done through two different methods: indication environment and direct instrumental sampling. Indicator environments allow assessing both dust and HM load throughout the city, disclosing geochemical peculiarities of HM anomalies in dust, while instrumental measurements are aimed at assessment dust content and spatial distribution of dust throughout urban areas. A picture of dust load distribution reflects pollution with coarse dust which deposits under the effect of gravity whereas airborne dust represents a mass of fine suspended particles.

The different aspects of atmospheric air pollution with dust may be assessed through different methods, the concurrent use of which allows obtaining comprehensive data about different aspects of pollution. Finally, this will serve as a basis for assessment of population health risks.

Investigations were carried out on a seasonal basis in 2011 through 2012 in the Center for Ecological-Noosphere Studies of NAS RA (CENS). Due to its sorption properties snow is a temporal depositing medium and provides information about short-term pollution [9], [14]. In summer similar indicator medium are leaves of arboreous plants [7].

Because of a limited budget, coherent sampling points (Figure 1) were selected from numerous mobile long-term monitoring sites (over 100) of CENS. Selection was based on 1) research data obtained earlier, 2) presence of probable pollution sources, 3) presence of persistent snow cover in winter months and its integrity within a sampling day, 4) presence of tree species required for carrying out sampling in summer, 5) maximal proximity of sampling points to residential sites.

Snow was sampled in compliance with the appropriate methods [9,14]. Snow samples were collected from plots with a defined area, placed into plastic containers and transported to the lab where the snow samples were melted at a room temperature and filtered; dry residue was then weighed. Dust and HM load in winter ( $P_w$  and  $P_{HM_w}$ ) was determined by formulas (1) and (2) [9]:

$$P_w = m_{dust} / S \cdot t \quad (1)$$

$$P_{HM_w} = C_{i\_snow} \cdot P_w \quad (2)$$

where  $m_{dust}$  is the sample dust weight;  $S$  – area of a sampling plot;  $t$  – a time interval between formation of a stable snow cover and sampling;  $C_{i\_snow}$  – concentration of an element in snow dust.

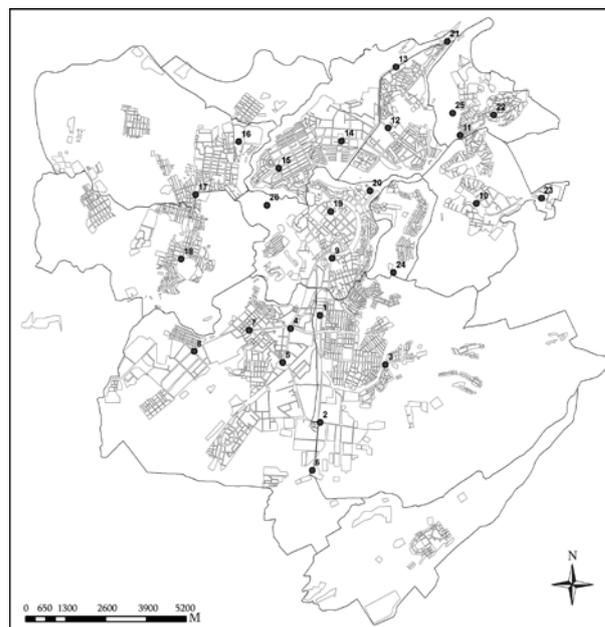


Figure 1. A map of location of sampling sites in Yerevan

Selection of plant species was done with regard for dust accumulation properties and prevalence in Yerevan area. The studied tree species were white elm (*Ulmus laevis*), Chinese elm (*U. parvifolia*), Persian walnut (*Juglans regia*), eastern plane (*Platanus orientalis*), and common lilac (*Syringa vulgaris*). Leaves were gathered at a max. height of 2 m above the ground, placed into paper bags and transported to the lab. Dust from leaf surfaces was washed out by distilled water, the generated liquid was filtered. A residue was dried and weighed. Dust and HM load in summer ( $P_s$  and  $P_{HM_s}$ ) was determined by formulas (3) and (4) [17]:

$$P_s = (m_{dust} - 0.35m_{dust}) / S \cdot t \quad (3)$$

$$P_{HM_s} = C_{i\_leaf} \cdot P_s \quad (4)$$

With a goal to assess HM contents in dust, dry residue was dissolved in nitric acid, then the acid was evaporated, and finally, to the residual solution de-ionized water was added until 20 ml was achieved. After that, the obtained solution was analyzed for concentrations of 11 chemical elements Hg, Cd, As, Pb, Cr, Ni, Co, Zn, Cu, Ag, Mo (ISO 9001) on AAS Analyst 800 [1].

A dust load level and a hazard degree of dust pollution of atmospheric air in winter and summer are assessed according to the N.S. Kasimov four-step scale provided in Table 1 [4].

Table 1. A four-step scale of dust load levels assessment [4]

Dust load level, kg/sq.km daily	Pollution level and degree of hazard
< 250	Low
250 – 450	Moderate, moderately hazardous
450 – 800	High, hazardous
> 800	Very high, extremely hazardous

A sanitary and hygienic assessment of the sites was done through collation between concentrations of chemical elements and their Maximum Acceptable Concentrations (MAC) in soils [5], as no MAC values for deposited dust have ever been developed. A level and degree of hazard of poly-element pollution of dust with HM was assessed based on the value of summary index of pollution (SIP) – an additive sum of excesses of actual concentrations of HM in dust vs. MAC (unit less), formulas (5) and (6) [5]:

$$SIP = \sum C_{i\_snow} / MAC \tag{5}$$

$$SIP = \sum C_{i\_leaf} / MAC \tag{6}$$

The levels of poly-element dust pollution with HM was assessed according to a five-step scale accepted in Armenia [5]

**Table 2. A five-step scale of assessment of levels of poly-element dust pollution with HM [5]**

SIP value	Pollution level and degree of hazard
< 8	Permissible
8 – 16	Low
16 – 32	Moderate, moderately hazardous
32 – 128	High, hazardous
> 128	Very high, extremely hazardous

Instrumental sampling of dust was done consistent with methods accepted in the RA [8] and using a portable aspirator ABA-1-120-02A. A certain volume of air was pumped through an AFA standard filter (a cotton fiber filter), then the filtrates were placed into paper bags and transported to the lab. Dust content was determined by weighing. Then collation was done between the obtained data and atmospheric dust standards accepted in the RA [6].

A set of relevant maps has been produced employing IDW methods and GIS ArcView software.

### 3. Results and Discussion

According to snow cover survey data, in winter the major part of the territory displays low levels of dust load (less than 250 kg/sq.km daily). However, against the background of a low dust load level, 21% of the studied samples displayed high level of dust load (varying 450-800 kg/sq.km daily). And finally 8% of samples displayed an extremely high dust load level (over 800 kg/sq.km daily). In the studied period, daily dust load averaged to 383.382 kg/sq.km (Table 3), this corresponding to a moderate degree of hazard.

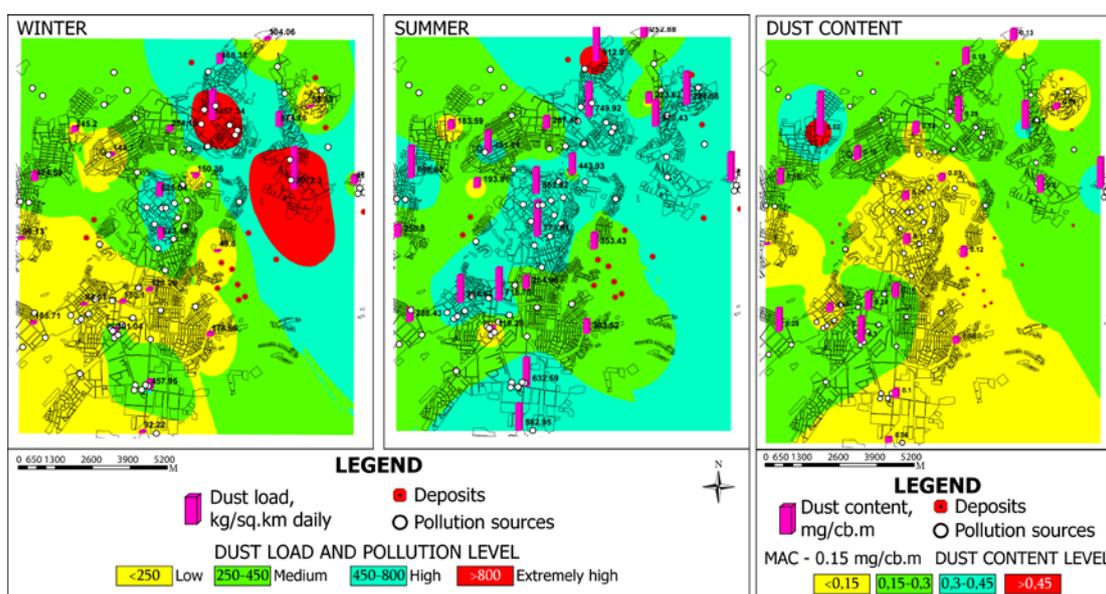
**Table 3. Descriptive statistics of dust load, dust content, HM total in winter and summer**

Parameter	Valid N	Mean	Median	Min	Max	SD
Dust load in winter, kg/sq.km	24	383.38	211.94	38.33	2072.3	473.82
Dust load in summer, kg/sq.km	25	471.37	491.81	110.28	912.89	227.53
Dust content in summer, mg/cub.m	24	0.175	0.143	0.003	0.518	0.12
HM load in winter, kg/sq.km	24	0.368	0.175	0.030	2.610	0.60
HM load in summer, kg/sq.km	25	0.972	0.340	0.090	14.940	2.92

In summer, a low level of dust load was established for 20, medium – for 32, high – for 44% of samples, whereas 4% of samples exhibited an extremely high level of dust load. In summer daily dust load averaged to 471.365 kg/sq.km daily (Table 3), that corresponds to a high degree of hazard.

As seen from provided data, dust load levels in winter vs. summer vary in a far more broader range, so a standard deviation in winter is almost twofold higher against a summer index (Table3).

Quite a different picture is observed in respect of summary load of HM. A range and standard deviation of this parameter is higher in summer (Table 3).



**Figure 2.** Dust load levels and dust contents in Yerevan atmosphere

As indicated by the research, in winter a mosaic-like distribution of dust load is common to the city (Figure 2).

The highest dust load level in winter is detected in the north and northwest of the city. Its central part is

characterized by a high level, in the southwest - by a low level of dust load. In summer vs. winter dust distribution throughout the city is of a more even character. Maximal values were established in the north of Yerevan (Figure 2).

In the southern and central parts of the city dust content is low and does not exceed MAC (0.15 mg/cub. m), while in the north, northeast and southwest the dust contents are high. Maximal peaks of dust were recorded in the northwest of the city. Mean dust content in Yerevan is 0.175 mg/cub. m (Table 3), exceeding the MAC 1.16 times.

In multifunctional cities such as Yerevan stationary dust sources are located rather dense, so it is hard to identify a dominant one. Nonetheless, considering distribution of man-made dust sources (including deposits noted above), directions of dominant winds (Figure 3) and frequently detected temperature inversions one may conclude that presumably, high dust contents in the north and northeast districts of the city and in near-earth layer originate under the impact of active deposits.

A mosaic character of dust load distribution in winter is determined by frequent calm weather (Figure 3). In summer, winds are more frequent, air movement is more intense. Consequently, this brings to a relative increase in dust load throughout the city.

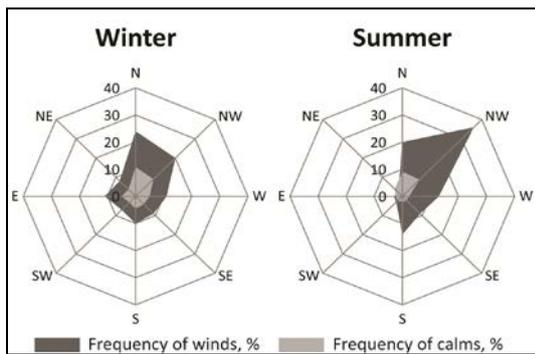


Figure 3. Frequency of wind directions and calm weather in Yerevan

Dust load distribution reflects pollution with coarse dust which deposits under the effect of gravity whereas dust content represents a mass of fine suspended particles. It is a cause, for which dust content and dust load in the

city area do not correlate ( $r = -0.134$ ;  $p = 0.541$ ). Yet, a significant correlation is detected between dust loads in winter and summer ( $r = 0.435$ ;  $p = 0.038$ ).

Both in winter and in summer in most parts of the city the HM load is low; the highest value of this parameter is detected in the south, housing three operating metalworking plants.

Generalizing the obtained research results, one may conclude that the southern part of the city is characterized by low and medium levels of dust load and high level of HM load in dust, whereas an opposite picture is observed in respect of the northern part of Yerevan: heavy dust load is accompanied by low load of HM. Central part of the city is characterized by high level of dust load (Figure 2) and medium level of HM load in both seasons.

One should note that partially, Yerevan dust is of natural origin. However, extremely high dust load levels and dust contents detected in the north and northeast of the city are formed presumably under man-made impacts emphasizing those produced by active tuff, basalt, clay and sand deposits. Heavy metals in atmospheric dust are of manmade origin.

The major share (over 50%) in a total load of HM falls on Zn and Cu in both seasons. In winter a sum mass fraction of Mo, Pb and Ni is also high. In summer Co and Cr deposition is more intense per unit area, their shares increasing at the expense of Pb, Ni and Mo. The level of load of most HM except Pb increases in summer. From the ecological viewpoint it is noteworthy, that in summer, Cd load and contents in dust increase (Figure 4).

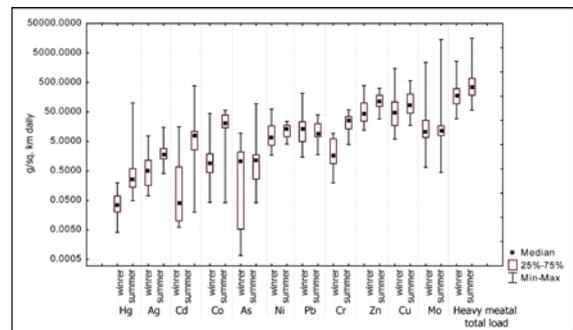


Figure 4. HM load in Yerevan

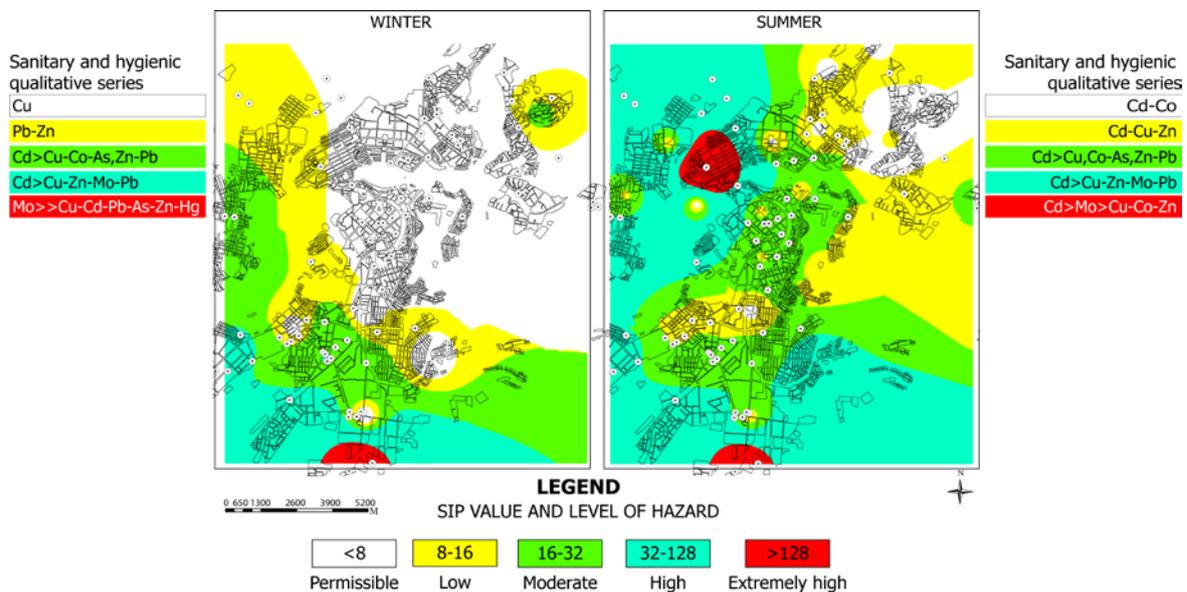
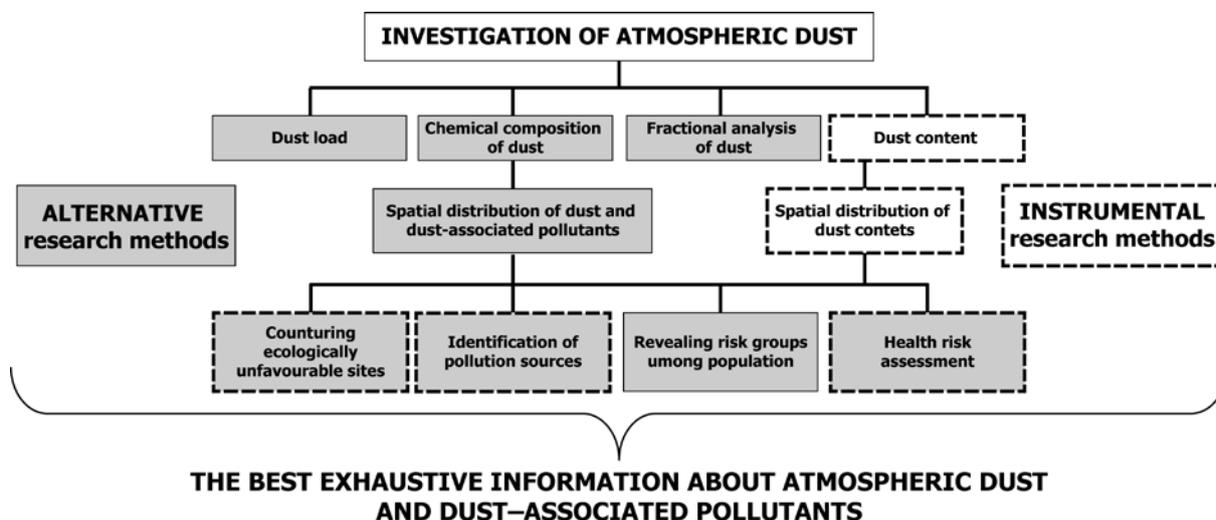


Figure 5. Levels of HM pollution

In winter, the major part of the city area is characterized by permissible and low levels of HM pollution (Fig. 5). The most intense pollution zone forms in the south of the city. Dominating pollutants in winter period are Pb and Cd, Mo being in the zone of extremely high pollution level. Commonly, in summer pollution levels are high throughout Yerevan, a dominant summer pollutant being Cd. The obtained results prove that a number of

metalworking plants located in the south of the city are a powerful source of HM and particularly of Mo, Hg and Cu.

So, a concurrent application of indicator mediums and instrumental measurements allows to mutually compensating disadvantages of separate atmospheric air research methods (Figure 6). This helps cover the most essential research aspects to obtain best informative parameters of eco-geochemical status of near-surface layer of urban air basins.



**Figure 6.** A conceptual scheme of a concurrent application of alternative and instrumental methods of investigation of atmospheric dust and associated pollutants on urban sites

## 4. Conclusions

Using alternative indicators allows assessing dust and HM load, deriving a picture of a spatial distribution of pollutants, providing eco-geochemical and sanitary and hygienic assessment of air pollution with dust and HM.

Using instrumental methods of research allows assessing dust content in the atmosphere and obtaining a picture of spatial distribution of dust.

A concurrent use of alternative and instrumental methods allows compensating disadvantages of separate methods and therefore obtaining the best comprehensive picture of pollution of near-surface layer of urban air, identifying pollution sources, contouring ecologically unfavorable sites, revealing risk groups among the population and assessing environmental and health risks.

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