Migration patterns of toxic volatile compounds in the atmospheric air of urban areas

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Abstract. The article presents the study results of the dynamics of persistent organic pollutants produced in the air during the decomposition of pesticide wastes. Analysis of the processes occurring in limited air volumes made it possible to establish patterns of changes in the concentration of such gases as hydrogen chloride and phosgene under the influence of a point source of their release. The obtained patterns complement similar studies conducted for more significant spatial scales.

1. Formulation of the problem
Due to the widespread application of persistent pesticides in the twentieth century, many countries are faced with the problems of disposal of pesticide wastes. Their long-term storage poses a threat to the natural environment due to high toxicity, the ability to migrate and persist for a long time in various living objects. At the Stockholm Convention of the United Nations in 2001 an international agreement was signed, which recognized the global threat of persistent organic pollutants to the world community. Among the most dangerous persistent organic pollutants are organochlorine preparations that are resistant to decomposition, especially, such as DDT, HCCCH and their isomers, the decomposition period of which is calculated in years. Despite their disposal, residual quantities have been partially buried, but most are stored.

Even when stored in metal tanks, organochlorine pesticides cause pollution of air and other objects with toxic gaseous products, primarily volatile toxic compounds, such as hydrogen chloride (HCL) and phosgene (COCL₂). Modern researches allow to reveal high concentrations of these substances, exceeding permissible levels both in the soil and in agricultural products.

2. Analysis of literature devoted to the considered problem
Numerous works have been devoted to the problem of studying the migration of disposed pesticide residues in various environments.

When studying the processes of interstructural migration of decomposition products of organochlorine pesticides in the “lithosphere-air” system, the works of B. Gevao can be noted [2]. According to the obtained results, the highest concentration values are noted for such substances as: dieldrin, pentachlorobenzene, hexachlorobenzene, oxychloride. The effect of the annual cycle of temperature on the concentration dynamics of these substances has been studied.
Y. Takazawa et al. established seasonal patterns of changes in the concentration of organochlorine preparations in the air at Cape Hedo (Japan) with a summer maximum and a winter minimum [9]. The patterns of the spatial migration of residual pesticides obtained by Y. de Souza Guida revealed the significant distribution of such substances as endosulfaan, cypermethrin, chlorpyrifos [1]. After a five-year study, M.Y. Tominaga determined patterns that made it possible to predict the concentration of pesticides in the air depending on a wide range of factors [10].

E. Holt studied the dynamics of organochlorine preparations in the air of buildings for various purposes [5]. As a result, a correlation between the concentration of pesticide residues in the air and the structure of the building was established.

The processes of migration of organochlorine preparations in water bodies are well studied on the example of large rivers in industrialized areas of the planet. For example, numerous data are available on the dynamics of organochlorine pesticide residues in the bed of the Yangtze River and Yellow River [4, 11].

Studies on the interstructural migration of organochlorine pesticide residues with the participation of living systems are being conducted. For example, numerous data on the migration of pesticide residues in the “soil-plant” system were obtained by the group of M. Silva-Barni [7, 8].

3. Goals, objectives and research methods
In the considered works, the dynamics of concentration on significant spatial volumes that are comparable to the size of cities, regions and whole regions was investigated [3, 6]. This approach does not always allow to obtain data for assessing the dynamics of the concentration field on small volumes, comparable to the size of the source of harmful substances.

The task of studying the migration processes in the air on small spatial scales of hydrogen chloride and phosgene, which are formed during storage of unused pesticide residues, was solved on the example of a warehouse located in the countryside. As shown by a preliminary inspection of the warehouse as a source of emission of harmful substances, pesticides are stored in partially leaking containers. For this reason, the processes of gas migration are considered on the territory of about 320 m². The obtained data allow us to study the field dynamics of concentration of volatile compounds, taking into account the size and location of the emission source.

In the process of research, twice a month for half a year, air was taken at points (pos. 1, figure 1) located at heights $h_1=0.2$ m; $h_2=1$ m; $h_3=1.5$ m at distances $l_1=0.5$ m; $l_2=4.0$ m; $l_3=10$ m from the warehouse in three coordinate axes (for example, X1 pos. 2). This made it possible to study the dynamics of the concentration of hydrogen chloride and phosgene in three mutually perpendicular surfaces A, B and C (for example, A – pos. 3).

Sampling was performed by the aspiration method. When studying the concentration of hydrogen chloride, 0.13 liters of air was pumped through two successively connected absorbers with a porous tube. When studying the concentration of phosgene of 0.05 liters, air was pumped for 10 minutes through two successively connected absorbers with a porous tube at a rate of 0.3 l/min. Alcoholic sodium hydroxide solution was previously added to each absorber.

Measurement of the mass concentration of hydrogen chloride and phosgene in samples of atmospheric air was carried out by the photometric method.
4. Discussion of the research results

The obtained results confirm the patterns of ambient temperature effect on the concentration of gases. The maximum concentration values were observed in the warm period of the year, and the minimum – in the cold one (Figure 2).

On the basis of the obtained results, planes illustrating the dependence of the concentration of hydrogen chloride and phosgene ($C = f (l, h)$), observed in July and November were built up (Figures 3, 4).

When analyzing the horizontal distribution of phosgene concentration (Figure 3, a; Figure 4, a), a more uniform field can be noted, which is associated with the high mobility of this gas. In the approximation of the dynamics of both gases, second-order polynomial dependencies were used. However, due to the features noted above, the equations describing the dynamics of the horizontal distribution of phosgene were fairly close to linear.

The distribution of the concentration of gases in the vertical direction is of great importance both from an environmental and hygienic point of view. In the open space, the release of hydrogen chloride and phosgene from the soil after processing it with organochlorine pesticides (OCPs), obeys the following pattern: the maximum amount of hydrogen chloride is determined in air layers at a height of 1-1.5 m, phosgene – at a height of 0.1-0.5 m from the earth’s surface. In the surface layer, near the warehouse, a circulation zone is formed, in which local areas with low pressure are formed, and therefore the concentration gradient in height is much smaller.
The maximum CHCL value in air is determined at \( l = 4.0 \) m independently for all values of \( h_1 = 0.2 \) m, which is due to the influence of turbulent air flow near the building. The minimum value of CHCL is fixed at \( h_2 = 0.5 \) m. With a value of \( l_3 \) the CHCL decreases by 11.2\% in comparison with \( l_2 \).

The minimum value of COCL\(_2\) is fixed at a distance of \( l_3 = 10 \) m; the maximum – in close proximity to the warehouse. The pattern of reducing the level of phosgene with distance from the warehouse is preserved when all heights above the ground are taken into account. Correlation analysis showed a close negative dependence of the phosgene content in the air on the distance to the storage place of pesticides, regardless of the sampling height: \( R = -0.99 \).

Thus, conducted studies have shown that the patterns of the horizontal distribution of hydrogen chloride and phosgene are in many respects opposite.

**Summary**

The article discusses the results of the study of gas migration processes on an area of about 320 m\(^2\), which is directly adjacent to the storage warehouse for disposed pesticides.

As a result of the research, the patterns of changes in the average concentration of gases by calendar months were established. The distribution analysis of the concentration of gases in the horizontal and vertical plane was conducted. The obtained data allow us to predict the dynamics of the considered gases in the air. As further data are accumulated, it is planned to build up prognostic mathematical models for a theoretical assessment of the effect of storage warehouse for disposed pesticides on agricultural facilities.
References
[1] de Souza Guida Y, Meire R O, Torres J-P M, Malm O 2018 Air contamination by legacy and current-use pesticides in Brazilian mountains: An overview of national regulations by monitoring pollutant presence in pristine areas *Environmental Pollution* **242** 19-30.
[2] Gevao B, Porcelli M, Rajagopalan S, Krishnan D, Martinez-Guijarro K, Alshemmarri H, Bahloul M, Zafar J 2018 Spatial and temporal variations in the atmospheric concentrations of “Stockholm Convention” organochlorine pesticides in Kuwait *Science of the Total Environment* **622-623** 1621-1629.
[3] Harner T, Pozoet K, Hung H, Caine J 2006 Global pilot study for persistent organic pollutants (POPs) using PUF disk passive air samplers *Environmental Pollution* **144** (2) 445–452.
[4] He C, Jin J, Xiang B, Wang Y, Ma Z 2014 Upper Yellow River air concentrations of organochlorine pesticides estimated from tree bark, and their relationship with socioeconomic indices *Journal of Environmental Sciences* **26** 593-600.
[5] Holt E, Audy O, Booij P, Melymuk L, Prokes R, Klánová J 2017 Organochlorine pesticides in the indoor air of a theatre and museum in the Czech Republic: Inhalation exposure and cancer risk *Science of The Total Environment* **609** 598-606.
[6] Shunthirasingham C, et al., 2010 Spatial and temporal pattern of pesticides in the global atmosphere *Journal Environment Monitoring* **12** 1650–1657.
[7] Silva-Barni M F, Gonzalez M, Silvia K, Miglioranza B 2019 Comparison of the epiphyte Tillandsia bergeri and the XAD-resin based passive air sampler for monitoring airborne pesticides *Atmospheric Pollution Research* **10** 33.
[8] Silva-Barni M F, Gonzalez M, Wania F, Lei Y D, Miglioranza K S B 2018 Spatial and temporal distribution of pesticides and PCBs in the atmosphere using XAD-resin based passive samplers: A case study in the Quequén Grande River watershed *Atmosphere Pollution* **9** 238–245.
[9] Takazawa Y, Takasuga T, Shibata S 2016 Recent decline of DDTs among several organochlorine pesticides in background air in East Asia *Environmental Pollution* **217** 134-142.
[10] Tominaga M Y, Silva C R, Melo J P, Niwa N A 2016 PCDD, PCDF, dl-PCB and organochlorine pesticides monitoring in São Paulo City using passive air sampler as part of the Global Monitoring Plan *Science of The Total Environment* **15** 323-331.
[11] Zhang L, Dong L, Yang W, Zhou L, Shi S, Zhang X, Niu S, Li L, Wu Z, Huang Y Passive air sampling of organochlorine pesticides and polychlorinated biphenyls in the Yangtze River Delta, China: Concentrations, distributions, and cancer risk assessment *Environmental Pollution* **181** 159-166.