Artículo de investigación

Transformation of the biogeochemical flows of mercury in the ecosystems of abandoned agricultural lands in Russia

Трансформация биогеохимических потоков ртути в экосистемах заброшенных сельхозугодий центра России

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Abstract

Using the methodology of critical loads, we studied the geographic peculiarities of changes in the natural stability of landscapes to mercury contamination through the atmosphere as a result of cropland abandonment; published the map of abandoned cropland in the central part of the Ryazan oblast as of 2015 (the materials are the courtesy of A.V. Prishchepov); identified and prioritized the main regional industrial emitters of mercury; estimated the average annual emission of Hg by industrial facilities of various types based on the specific features of the production; and showed that the most contrasting impact is associated with the activity of a cement manufacturer (a combination of notable amounts of involatile Hg emission and the relatively low height of industrial chimneys (120 m)); and found that the colonization of abandoned land with woody vegetation covers only small-area windless regions of the forest already existing in the territory, which determines the overall deterioration of resistance to Hg supply. We also noted that abandoned lands feature favorable conditions for the sedimentation of anthropogenic pollutants migrating in the atmosphere, which among other factors causes an increase in the concentration of biologically available forms of Hg in post-agrogenic soils by 1.5~1.8 times compared to the arable land and normal soil under forest ecosystems. We detected a local but contrasting anomaly of Hg in the tissues of post-agrogenic woody plants, where the mercury content exceeded the background levels by 20–200 times. It was noted that post-agrogenic

Аннотация

С использованием методологии критических нагрузок изучены географические особенности изменения естественной устойчивости ландшафтов к ртутному загрязнению через атмосферу под влиянием забрасывания сельхозугодий. Публикуется карта заброшенных земель в центре Рязанской области по состоянию на 2015 г. (материалы любезно предоставлены А.В. Прищеповым). Установлены и ранжированы по степени приоритетности основные региональные промышленные эмитенты ртути. Рассчитана среднегодовая эмиссия Hg промышленными объектами различных типов исходя из специфики производства. Показано, что наиболее контрастное импактное воздействие связано с деятельностью цементного предприятия (сочетание заметных объемов эмиссии Hg в труднолетучих формах со сравнительно небольшой высотой промышленных труб – 120 м). Выявлено, что зарастание заброшенных земель древесной растительностью охватывает лишь небольшие по площади ветровые тени уже имеющихся на территории лесных массивов, что определяет общее снижение устойчивости к поступлению Hg. Также отмечено, что на заброшенных землях складываются благоприятные условия для осаждения техногенных загрязнителей, мигрирующих в атмосфере, что в числе иных факторов приводит к росту концентраций биодоступных форм Hg в постагрогенных

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ecosystems are less resilient to anthropogenic chemical pollution and their adaptation mechanisms are more likely to fail. In the study of the dispersion halos of technogenic Hg, the wood, bark, and branches of birch, being a common plant component of abandoned lands, should be recognized as the indicating biological objects.

Keywords: Biogeochemical anomalies, abandoned land, critical load method, mercury, technogenic pollution through the atmosphere

почвах в 1,5-1,8 раза относительно пашни и зональных почв под лесными экосистемами. Выявлена локальная, но контрастная аномалия Hg в тканях постагрогенной древесной растительности, где содержание ртути превышает фоновые уровни в 20-200 раз. Отмечено, что постагрогенные экосистемы обладают сниженной резистентностью к антропогенному химическому загрязнению и высокой вероятностью срыва адаптационных механизмов. Индикаторными биообъектами при изучении ореолов рассеяния техногенной Hg следует признать древесину, кору и ветви березы — распространенного растительного компонента заброшенных земель.

Ключевые слова: биогеохимические аномалии, заброшенные земли, метод критических нагрузок, ртуть, техногенное загрязнение через атмосферу

Introduction

Abandonment of agricultural land is a multi-factor socioeconomic phenomenon that is very widespread in the countries of the former USSR, particularly in Russia (Prishchepov et al., 2012). For example, in the last 20 years in the center of the Ryazan region 35% of agricultural land has been abandoned (for various reasons) (Figure 1); this figure tends to decline, but at a slow pace.

Even in the 21st century, mercury (Hg) remains one of the least studied elements, whose background content in landscapes has not been even reliably estimated (Perelman and Kasimov, 1999). At the same time, Hg, having the maximum affinity for air migration, is an indispensable companion of natural and anthropogenic geochemical anomalies (Kovalevsky, 1991) and, therefore, has an indicative value. This publication discusses some geochemical and landscape-related aspects of abandoned cropland pollution with mercury.

Research subjects and methods

The research area is a model site within the territory of one of the typical regions of the center of the East European Plain, the Ryazan oblast, within 50~60 km from the regional center. This site is the geochemical focus of the entire region, because, firstly, it contains all the main soil-geochemical conditions of the central part of Russia and has the most contrasting geochemical boundaries, and secondly, the main industrial emitters and the impact zones of their emissions are located within this territory.

The area of the research site is 1900 km^2, of which 41.5% falls on the area of sandy and light loamy soils of the Meshchera lowland (where woodland and marshy ecosystems predominate), 51.5% is the share of the landscapes of the Oka-Don lowland and Central Russian upland, where middle and heavily loamy soils, mostly plowed, prevail (including 2% being the territory of the city of Ryazan), 7% is the area of the Oka and its largest tributaries' floodplains. The largest massifs of abandoned lands are found in the southern Meshchera and in the north of the Oka-Don lowlands (Figure 1).

In February–March 2015, we tested the main landscape components (snow cover, soil humus horizons, woody vegetation, surface water) in the ecosystems of abandoned lands (the sampling points are shown in Figure 1); the mercury content in the samples was determined by the cold vapor method using a Spectr-5-4 atomic absorption spectrometer. Mercury was extracted from the soil samples with an acetate-ammonium buffer solution with pH=4.8 (simulating the response of the cell sap of the plants' root hairs and transferring the most bioavailable forms into the solution).

To determine the reserves and increment of wood with bark on the abandoned cropland and burnt wood, we used the middle tree method and the known patterns of the growth of birch, pine, and aspen tree stands of the central part of Russia (Usoltsev, 2002); the density of tree stands was determined by an expert method by counting woody plants at test sites and analyzing high-resolution multispectral satellite images (1 m per pixel).

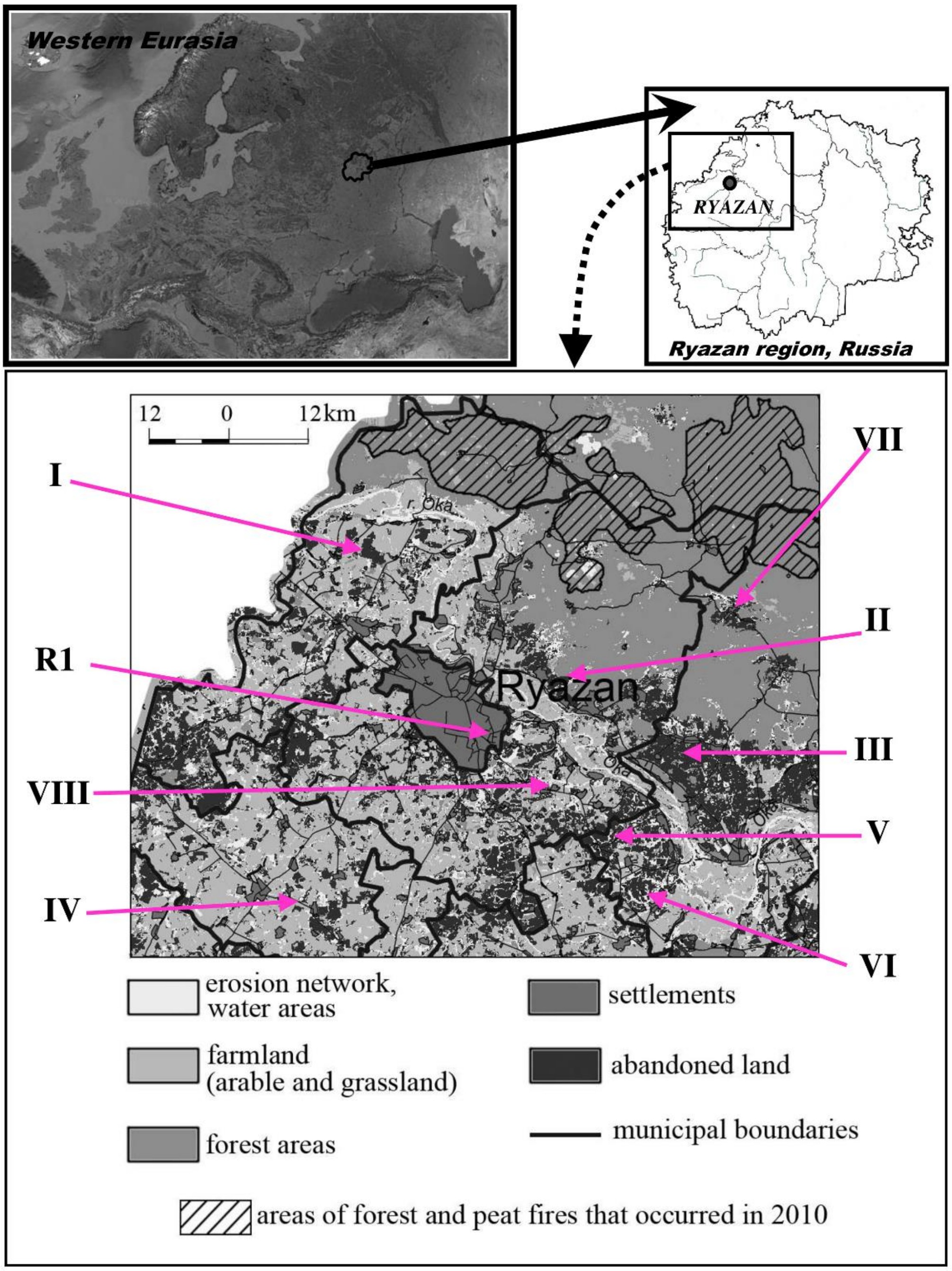

Figure 1. The structure of the land reserves of the research area—the central part of the Ryazan oblast (compiled based on materials provided by A.V. Prishchepov (Prishchepov et al., 2012))*

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Notes. Hereinafter, I–VIII are the points of biogeochemical testing in the abandoned lands, R1 is the point of testing woody vegetation (55-year-old silver birch *Betula pendula*) within the medium radius of impact of non-ferrous metallurgy enterprise.

I. Central Russian upland, middle loamy soils; unexploited fruit-tree forests surrounded by birch forest belts;
II. Meshchera lowland, sandy soils, overgrown with pine (*Pinus sylvestris*);
III. Meshchera lowland, light loamy soils, overgrown with birch (*Betula pendula*, *B. pubescens*);
IV. Central Russian upland, heavy loamy soils (chernozems), overgrown with birch;
V. and VIII – Oka-Don lowland, middle loamy soils; overgrown with birch;
VI. in the same place, 9 km southeast of Point V, overgrown with birch;
VII. Meshchera lowland, light loamy soils, overgrown with pine and birch;

R1 – the birch garden square in the southern industrial district of Ryazan.

*the types of land use are mapped based on the results of interpretation of satellite data of remote Earth's surface sensing.

We analyzed the obtained data by the widespread (especially in the European Union) method of critical loads – CL method (UNECE Convention, 2004). The CL method determines the upper limits of pollutant supply to the ecosystem, which are the maximum pollutant amount that does not violate the natural geochemical balance. Ecological regulation of pollution based on the CL method is a more advanced approach to environmental management, compared to traditional hygienic regulation, which is based on the “anthropocentric” MAC concept that does not take into account the diversity and spatial mosaic pattern of the assimilation potential of ecosystems (Bashkin, 1997).

There are three remediation mechanisms for the contaminants polluting landscapes (especially when they come from the atmosphere and cover the entire area of the ecosystem (Krivtsov et al., 2011)): absorption by vegetation (M_{upt}); leaching with surface and ground runoff (M_{runoff}); and accumulation in immobilized forms in the soil ($M_{SD(acc)}$). At the same time, the anthropogenic influx of pollutants into landscapes should be fully compensated by the process of natural remediation:

$$CL = M_{dep}^{max} = M_{upt} + M_{runoff} + M_{SD(acc)}. \quad (1)$$

The accumulation of heavy metals in wood biomass is calculated as:

$$M_{upt} = G_{an} \times C_{back\,M}, \quad (2)$$

where G_{an} is the annual production of woody biomass, C_{backM} is the concentration of an element in a particular biomass fraction that is safe for humans and natural landscapes. C_{backM} is the environmental standard for forest ecosystems, determined based on the results of biogeochemical testing using variational analysis procedures (Puzachenko, 2004) (the priority is to preserve the natural chemical equilibrium), and when assessing the assimilation potential of agrocenoses, MAC is used as $C_{back\,M}$ (prioritizing the preservation of human health). In the background areas with no forests, M_{upt} is not taken into account because the fixation of elements in herbaceous plants is temporary (Protection of Nature, 2004). The algorithms for calculating the parameters M_{runoff} and $M_{SD(acc)}$ are provided in our monograph (Krivtsov et al., 2011).

A characteristic feature of the research site is the presence of fairly stable long-term average paths of the aerial migration of anthropogenic toxicants (Figure 2). These paths are formed under the influence of two main factors (interconnected through the process of dynamic turbulence): circulation factor (Ekman transport: right-handed rotation of the vector of man-made emissions plumes velocity as the altitude increases), and geomorphological factor (the channeling effect of the Oka floodplain) (Krivtsov et al., 2011). Thus, the paths of technogenic emission dispersion are quite definite and predictable, and some of the studied post-agrogenic ecosystems (for example, Point V) turned out to be confined to the places of intersection and summation of the migration paths of the emissions of different industrial emitters.

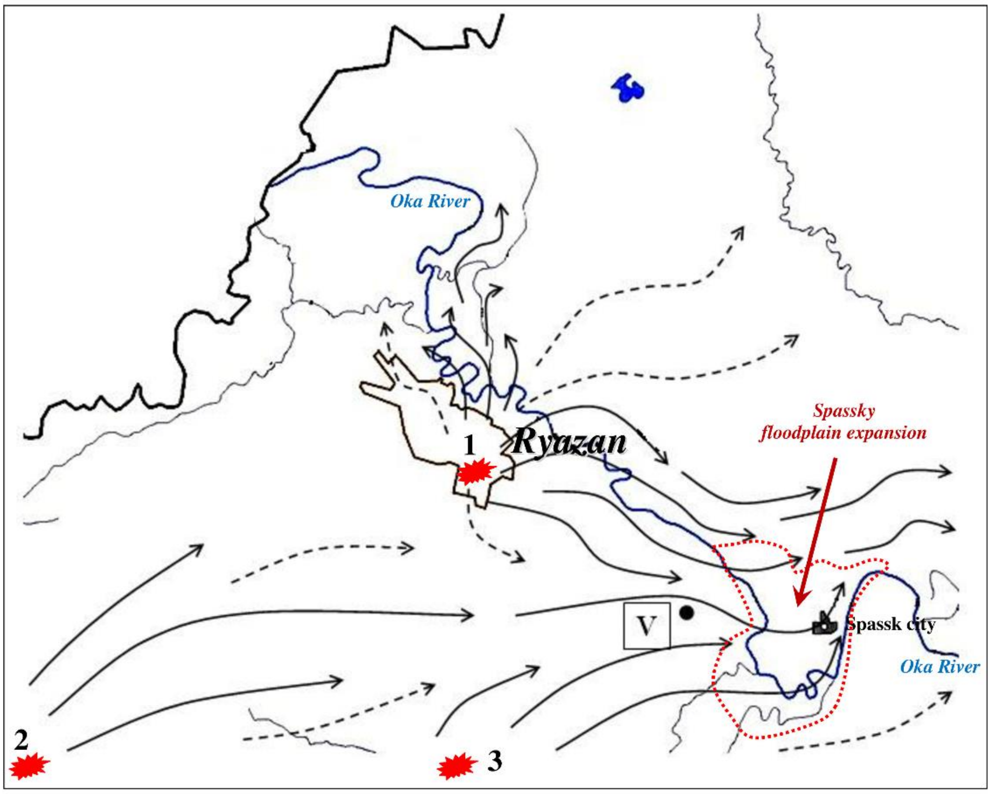

Figure 2. Conditions for the atmospheric migration of pollutants in the center of the Ryazan oblast (Krivtsov et al., 2011)

Note: the solid arrows are the long-term average paths of air transport of pollutants; dashed arrows are the "secondary" paths of the technogenic impact.

The localization of Point V with abnormally high concentrations of Hg in the woody vegetation of abandoned lands is shown.

The Spassky expansion of the Oka floodplain (the lowest geomorphological element) is a "technogenic geochemical focus" of the entire research site.

The main sources of technogenic emission of Hg are:

1. The Southern industrial hub of the city of Ryazan;
2. Mikhailovtsement CJSC (outside the research site);
3. The Ryazan State District Power Plant (outside the research site).

Results and discussion

Abandonment of agricultural land, which is very widespread in the center of the Ryazan oblast (Figure 1), is one of the factors modifying the biological cycles of elements. To maintain geochemical stability at a constant level, it is important to ensure a complete compensation of the lack of elimination of toxic elements with harvests on the abandoned lands with long-term accumulation in wood during their natural overgrowing with plants. However, such compensation does not occur, since the process of overgrowing is rather slow, probabilistic, and strongly depends on wind direction and speed, as well as the wind-breaking properties of the woody vegetation. As shown in Figure 3, it mainly covers the windless regions, already existing in the territory of forest areas and forest belts (frontal and rear)), and reduces greatly already at a distance of 10~20 heights of crowns of the trees producing seeds.

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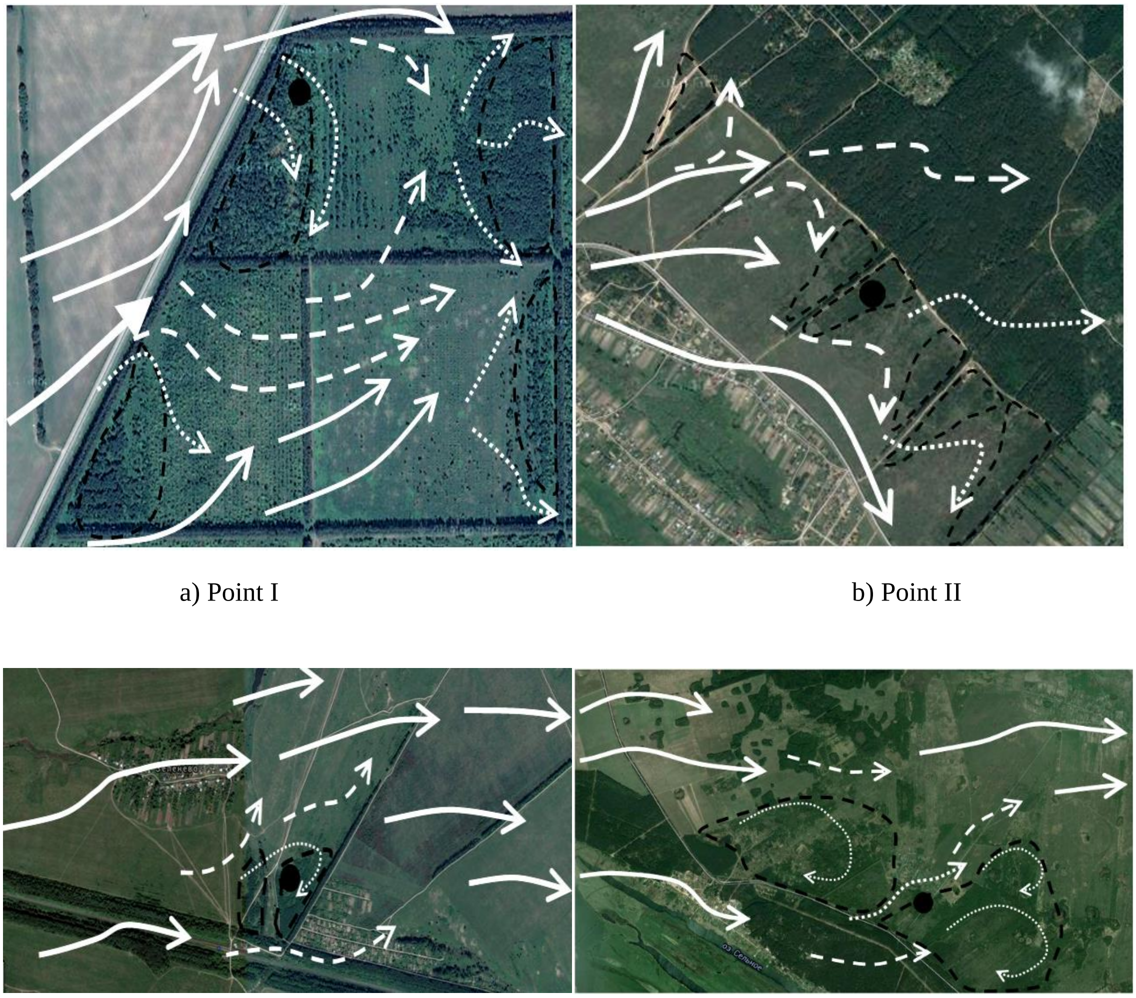

a) Point I b) Point II

c) Point VIII d) Point III

Figure 3. Attenuation and deviation of air flow by woody vegetation, as a factor of abandoned land overgrowing by plants

Note: The black dotted lines outline the windless regions. The solid white arrows show the main paths of high-speed transit air transports; the dashed white arrows show air currents weakened and deflected by friction. The black circles indicate the location of biogeochemical testing points (bark, wood, branches, needles).

As can be seen from the figure, small areas that are most screened by old vegetation from prevailing winds, where seed accumulation is most likely, are exposed to active overgrowth. The processes described above cause a situation where 90% of the abandoned lands of the research site still have a disappearingly low density of tree stands (Figure 4), and areas with a tree stand density above 0.2 (very rarely up to 0.7–1.0) are limited to locations, although they can be found in some places (Tobratov, Zheleznova and Vodorezov, 2018).

Figure 4. Sampling site II: the general view of an overgrown field

Note: in the background, there is a local zone of active overgrowth in the windless region behind a pine forest belt (marked by arrows).

Thus, in the abandoned lands of the Ryazan oblast, currently there are adjacent sites with significant density of young tree stands and areas overgrown with only grassy vegetation with single trees as an exception, and the latter areas being absolutely predominant in size. The accumulation of toxic elements (including Hg), which are not removed with the harvest, in herbs is temporary ("recycling accumulation"), and, therefore, this accumulation is not taken into account when calculating CL (Protection of Nature, 2004). Thus, the slow rate of colonization of post-agrogenic areas by woody vegetation should be considered as an environmentally unfavorable phenomenon.

Moreover, stands of the "filtering" type—with a free openwork structure, significant gaps between the clumps of trees, and without dense edges—are formed on abandoned lands in the process of uneven overgrowing (Kurbatova and Gribkova, 2006). Consequently, the overgrown areas of abandoned land act as atmospheric "filters", more efficient than closed forests.

In this regard, the clearly expressed accumulation of mobile forms of Hg in post-agrogenic soils in comparison with not only arable ones (which is quite natural (Gordeeva, Belogolova and Andrulaitis, 2012), but also with zonal undisturbed soils (under forests), observed independently of the provincial and landscape conditions and to the north and south of the Oka River (Table 1) seems to be a non-accidental phenomenon. Values of r_W are quite low due to the mosaic pattern of the natural and anthropogenic geochemical environment in the old-cultivated region (for most natural objects, it is rather a rule than an exception (Uchvatov, Mitusov and Kalachikova, 2006), but the differences between soil groups are statistically significant at a high level of confidence (α<< 0.05) (Puzachenko, 2004). Exclusion from the analysis of the data array representing abandoned lands showed the absence of significant differences in the mean values of the other groups (α= 0.10–0.15).

Thus, abandoned lands are the place where the most favorable conditions for the accumulation of bioavailable mercury are currently developing. As shown below, such accumulation occurs under the influence of an increase in the Hg aerial flow in combination with changes in the humus content of soils after their removal from circulation. At the same time, the low rate of woody vegetation overgrowth does not ensure the proper rates of immobilization of the excessive mobile forms of Hg in the incrementing wood (as in old-aged forests), and soil becomes their main accumulator, which, in particular, determines the high statistical significance of the differences between the date groups presented in Table 1.

Table 1. The results of the analysis of variance for the content of mobile forms of mercury (C_{Hg}-*mob**) in soils, depending on landscape conditions and land use type

LAND CATEGORIES	*loamy soils* **				*sandy soils* ***			
	X	σ_z^2	α	r_W	X	σ_z^2	α	r_W
Abandoned agricultural land	4.32	0.52	0.002	0.114	4.26	1.84	0.019	0.149
Forests	2.86	1.09			2.79	1.99		
Arable soil	2.39	1.41			–	–	–	–
Erosion network	2.97	2.98			–	–	–	–

Notes: X is the average value of C_{Hg}-*mob*. µg/kg; σ_z^2 is the intragroup dispersion, µg/kg; α is the significance level (the null hypothesis is rejected at α <0.05); r_W is the intraclass correlation coefficient characterizing the influence of the factor (in this case, grouping by soil types) on the productive indicator (in fractions) and is calculated by the following formula:

$$r_W = \frac{\sigma_A^2 - \sigma_Z^2}{\sigma_A^2 + (n_c - 1) \times \sigma_Z^2} \quad (3)$$

where σ_A^2 and σ_z^2 are, respectively, the factorial and random (intragroup) variance of the concentration values, n_c is the average volume of gradations of the factor under study.

* The extractant is an acetate-ammonium buffer solution with pH=4.8 (forms that are potentially available for root absorption).
** Landscapes of zones of deciduous forests and forest-steppe (areas south of the Oka River).
*** Landscapes of the zone of mixed forests of the Meshchersky natural province (areas north of the Oka River).

The map-scheme in Figure 5 clearly shows two main sources of precipitation pollution with mercury: the industrial complex of the city of Ryazan (secondary) and the cement production in the Mikhailovsky district (main). The emission factor of Hg in the production of cement in CIS enterprises is 0.013–0.014 g/t of finished products (Kuzmin et al., 2012), which with the production capacity of Mikhailovtsement CJSC equal to 2.154 million tons per year (Kuznetsova, 2013) leads to the annual emission of 29.68 kg of Hg by the enterprise (there are higher estimates: 39 kg (Yanin, 2004b) and even up to 81 kg (ACAP, 2005) in 2001).

Despite the high volatility of mercury (Meteorological Synthesizing Centre, 2012), its main part emitted by the said enterprise, being directly or indirectly associated with cement dust, does not become a part of global migration and is deposited in the landscapes of the impact zone of the emission source. This is facilitated by the confinement of the bulk amount (over 90%) of Hg in the emissions of cement enterprises to relatively coarse aerosols (Yanin, 2004b) with a characteristic lifetime in the atmosphere of less than 10 days (versus 0.4–3.0 years for the atomic form (Kalinchuk, 2016)), as well as the relatively small height of the chimneys of the enterprise and the widespread development of "all-weather" inversion stratification of the surface atmosphere in winter seasons (Figure 6). As a result, a local technogenic anomaly of the Hg content in the snow cover has been formed northeast of the enterprise (Figure 5), which most contrastively manifests itself on the abandoned lands overgrown with "filtering" vegetation—sparse birch forests.

At the same time, the contrast of the atmospheric hydrochemical mercury anomaly in the snow cover in the vicinity of the city of Ryazan turned out to be noticeably lower than near the Mikhailov settlement. This is due to the objectively lower emission of Hg by the enterprises located in the regional center. The largest industrial emitters of Hg in Ryazan are RNPK JSC (oil refinery) and Ryaztsvetmet CJSC (non-ferrous metallurgy enterprise: production of secondary lead in the processing of automotive batteries). Industry average data provided in surveys (ACAP, 2005; Yanin, 2004a) (in particular, the approximate value of the specific emission of Hg in the smelting of secondary lead is about 0.2 g/t of the resulting metal) estimate with a certain degree of uncertainty the total technogenic emission of mercury into the atmosphere of the regional center at 19.0 kg/year (including 12.5 kg from RNPK JSC, 5.0 kg from Ryaztsvetmet CJSC), which makes only 64% of the emission level of Mikhailovtsement CJSC.

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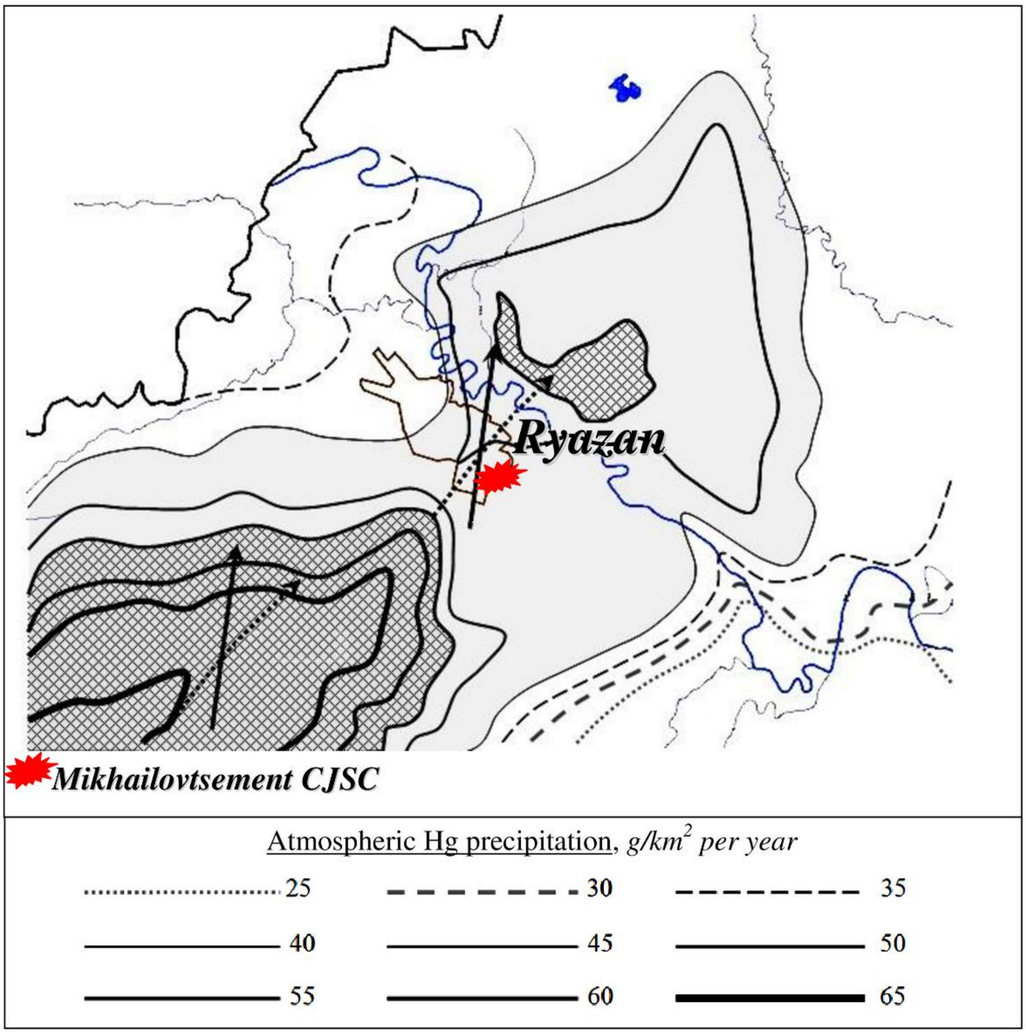

Figure 5. The “technogenic axis” of atmospheric mercury migration in the center of the Ryazan region, identified by snow surveys on abandoned agricultural lands (the snow cover was tested on 03.03.2015)*

Notes.

1) When calculating the annual amount of Hg precipitation for the atmospheric supply of the winter period, we used standard methodological approaches (Glazovsky, Zlobin and Uchvatov, 1978).
2) The areas of atmospheric supply of Hg over 40 g/km^2×year (technogenic impact indicators) are filled with light gray color, over 50 g/km^2×year (regional peaks of Hg supply) are marked by hatching.
3) The arrows show the average seasonal wind directions in the winter of 2014–2015: solid arrows indicate wind in the surface atmosphere (at the level of the weathervane), dotted arrows indicate wind in the free atmosphere (beyond the boundary layer). The mismatch of transport directions is due to the influence of the Ekman circulation.

❖ The map-scheme is representative only for abandoned croplands.

Figure 6. Mikhailovtsement CJSC: a descending stream of emissions with an anticyclone inversion and southwestern wind

The Ryazan State District Power Plant still holds the lead in Hg emissions, especially after the planned change in the fuel balance of this power plant. Currently, the share of coal in the fuel balance of the power plant has almost doubled compared to 2013 and exceeded 57% (the natural consumption is 1.8–2.1 million tons per year (Annual Report of PJSC OGK-2 for 2016, 2017)). Using industry average data (Yanin, 2004c; Kuzmin et al., 2012; ACAP, 2005), it is possible to determine the approximate scale of Hg emission by this enterprise: in recent years, it has ranged within 118–136 kg/year – with the emission factor of 0.065 mg of Hg per 1 kg of power generating coal and 0.0014 mg per 1 m^3 of natural gas (Yanin, 2004c; Mercury pollution in Russia, 2016).

However, the ecological significance of these seemingly high volumes of atmospheric Hg emission is effectively compensated by the high height of the chimneys of the State District Power Plant (2.5 times higher than those of Mikhailovtsement CJSC), which, in turn, entails a six-fold decrease in the maximum surface concentration of technogenic impurities due to atmospheric scattering (Berland, 1975). In addition, Hg in the emissions from thermal power plants enters the environment mainly in highly volatile gaseous form, including atomic Hg^0 (not as aerosol, as in cement production (Yanin, 2004c)), which, due to its relative chemical inertness and extreme volatility, diffuses beyond the boundary layer into the middle troposphere, where it migrates for tens of thousands of kilometers (Kalinchuk, 2016).

Consequently, Hg emission at the Ryazan State District Power Plant has a pronounced macro-regional and global nature, while Mikhailovtsement, on the contrary, impacts locally and forms a “technogenic axis” of atmospheric mercury dispersion (Figure 5).

Given fairly conflicting data on the actual level of atmospheric supply of Hg in the central part of the East European plain, according to one of the most reliable estimates (Meteorological Synthesizing Centre, 2012), its background level in recent years has been 20–25 $g/km^2 \times year$ against the slow decline tendency. The rate of decline is by an order of magnitude lower than, for example, that of Pb and even Cd due to the high volatility of Hg, the global nature of its atmospheric migration, and its growing emission in developing countries in Asia and Latin America; and the growth of coal combustion at the local source of background pollution—Ryazan State District Power Plant—also contributes to it. In the course of our studies, close-to-background values of the atmospheric supply of Hg were recorded only at Point I and Point VI. The remaining points were within the outline of the “technogenic axis of air migration” (Figure 5), and the supply of Hg to them turned out to be 1.5–2.5 times higher than the background values given in publications. Thus, the supply reaches the levels typical of the main industrial regions of Europe: the Moscow oblast, Southern Poland, North Rhine-Westphalia in Germany, etc. (Meteorological Synthesizing Centre, 2012); in the open spaces of arable land, it is closer to the background values.

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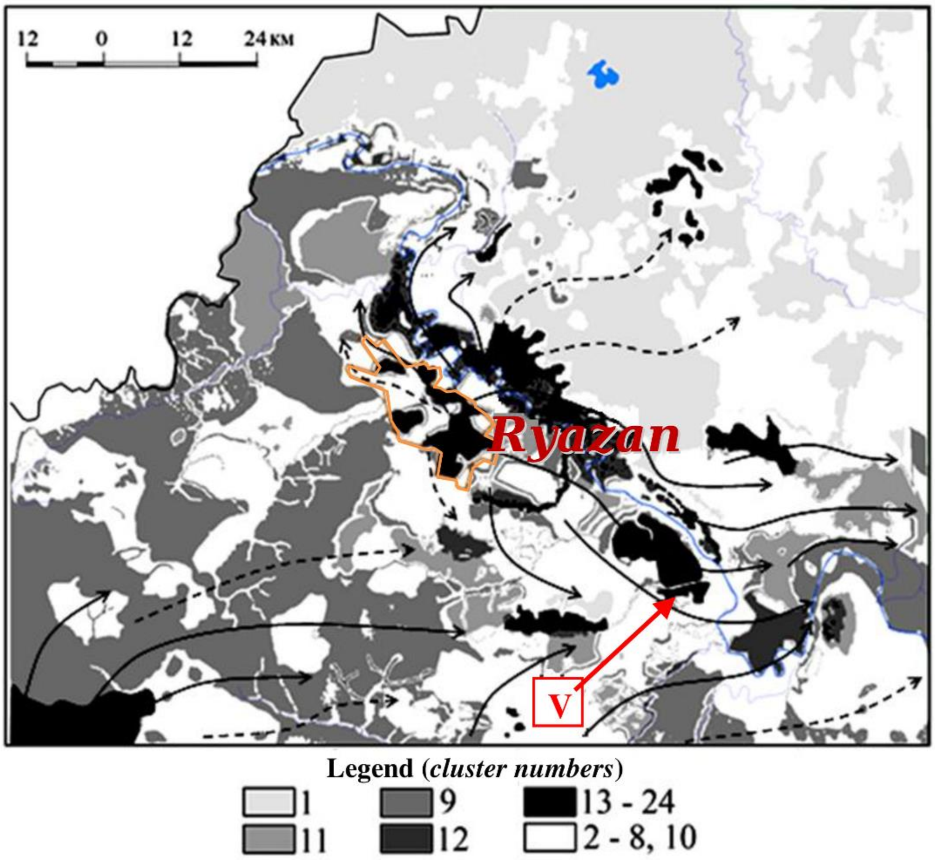

Cluster 1 is the background of sandy and peat soils in Meshchera Lowland.
Cluster 11 is the background of light loamy soils.
Cluster 9 is the background of medium and heavy loamy soils (chernozems and gray forest soils).
Cluster 12 is the background of floodplain accumulations.
Clusters 13–24 are the areas of technogenic pollution of soils with heavy metals.
Clusters 2–8 and 10 are genetically heterogeneous.

Figure 7. Areas of background and technogenic soil-geochemical conditions in the center of the Ryazan oblast according to the results of a cluster analysis for mobile forms and total concentrations of Cu, Zn, Pb, and Cd

Note: the arrows indicate the average annual paths of the technogenic impact formed under the influence of the relief (see Figure 2).

At the same time, the *long-term average annual* spatial pattern of technogenesis in the center of the Ryazan oblast is somewhat different: with a share of winds in the western quarter greater than in 2015, the paths of air migration of pollutants deviate to the east and southeast, and the “aerodynamic channel” of the Oka floodplain functions (Figure 7). In the territories adjacent to this channel, the aerial technogenic pollution of the landscapes is most likely, and the Spassky floodplain expansion acts as a collector of emissions by the main regional emitters (Krivtsov et al., 2011). The response of landscapes to pollution is spatially heterogeneous (mosaic): the technogenic supply of pollutants is most stably responded to by the tracts of lowland marshes in Meshchera, by the tracts of inter-ridge depressions and transgressing terrace floodplains in the Oka floodplain, and by kettles, slope feet, as well as abandoned farmlands in the Oka-Don lowland.

One of the largest abandoned land masses in the region (testing Point V) is located at the intersection of the prevailing air routes of pollutant transport. It was within its limits (Figure 7) that we revealed one of the regional peaks of the soil concentration of mobile (accessible for root absorption) forms of Hg: 5.23 μg/kg, which is 1.2 times higher than the average value in the humus horizons of the abandoned lands south of the Oka River, and 2.2 times higher than that in the arable loamy soils (Table 1). But the most significant fact is that we recorded "hurricane" concentrations of Hg in the phytomass of woody plants in Point V, even in trunk wood (Table 2). Apparently, Point V is a good example of plants' "failure to adapt" to anthropogenic impact. This is also facilitated by the presence of the air migration of toxicants within the main regional channel, and the "filtering" nature of vegetation, typical of overgrown areas of abandoned fields, which aggravates consequences of technogenesis.

Of note, it is extremely difficult to assess the ecological state of ecosystems in Point V within the framework of traditional hygienic standardization procedures. For Hg, being a poorly studied element, there is no reliable estimate of its background concentrations in soils; MACs have been determined only for its gross content, but not for the most environmentally significant mobile forms (GN 2.1.7. 2041-06, 2006). The MACs of Hg in food items have been determined, but it is inappropriate to use hygienic standards for estimating mercury concentration in the phytomass of woody plants, since they are not food items and are not of direct interest to humans. It turns out that hygienic regulation is not able to provide any adequate assessment of the negative phenomena that can occur on farmlands after they have been taken out of circulation, since it is carried out from a "selfish" standpoint of usefulness or harmfulness to humans, and ecosystemic criteria of the environment state do not apply in this case (Bashkin, 1997).

Table 2. The concentration of mercury in the tissues of post-agrogenic woody plants at different points of biogeochemical testing (the samples were taken on 18.02.2015 and 03.03.2015, the prevailing age of plants was 6–18 years)

Testing point	*Hg concentration, μg/kg of air-dry phytomass*			*Plant species*
	wood	*trunk bark*	***branches***	
II	9.56	12.65	10.15	*Pinus sylvestris*
III	8.71	9.88	14.86	*Betula pubescens*
IV	4.90	8.42	9.37	
V	267.10	553.61	2056.74	*Betula pendula*
VI	9.03	11.30	7.63	
VII	5.12	10.96	10.02	*Betula pubescens*
R1	6.84	18.25	42.55	*Betula pendula*

Therefore, the ecological and geochemical processes in the ecosystems of abandoned lands can be analyzed exclusively by the critical load method. As follows from the above mass balance equation (1) and formula (2), a necessary step in such an analysis is to study the biogeochemical flows of toxicants. Table 3 shows the regional average ecosystemic assessment of the biotic transformation of Hg and the contribution of abandoned lands to this process.

As can be seen from the table, this contribution is extremely low due to the low speed and irregularity of their overgrowing with woody vegetation: when the concentrations of mercury in wood of zonal forest ecosystems, abandoned lands, and in cultivated plants are similar, it is the low density of tree stands that determines a 30-fold decrease in the biogeochemical resistance of abandoned lands to Hg supply, compared to agrocenoses, and a 5-fold decrease even compared to the overgrowing burnt woods of the Meshchera Lowland (Table 3). *Individual trees* in abandoned lands develop (especially grow in thickness) much better than in zonal forest

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ecosystems (Table 4), with the exception of thickened tree stands on low-trophic substrates (Point III), but the factor of *average density* is more important.

Table 3. The role of various categories of land in the biogeochemical flows of mercury in the natural and anthropogenic landscapes of the Ryazan región

Categories of land	*Share in the area of the research site, %*	*G_{an}, t/km²/yr*	*C_{Hg}, µg/kg*	*Average tree stand density*	*Hg_{upt}, g/km²/yr*	*Share in the total biogeochemical remediation of mercury, %*
Forests	24.0	145.6	11.66	0.657	1.697	19.2
Forests damaged by fire in 2010	11.6	60.3	8.62	0.5–0.8	0.520	2.9
Abandoned farmland	12.5	10.6	9.09*	0.038	0.096*	0.6*
Arable land	49.5	459.4	6.99	–	3.211	76.8

Note: G_{an}, C_{Hg} and Hg_{upt} are the parameters of equations (1) and (2).
*excluding data for Point V.

However, for Hg, the biotic component of resistance is only about 5% of the critical load (the abiotic mechanisms of rehabilitation predominate), which is due to its low biophile properties and the barrier-type absorption by the majority of plants (Figure 8). However, the barrier mechanisms that prevent the biological absorption of mercury do not always function efficiently. An example of their failure is Point V (Table 2), where our biogeochemical testing revealed intensive accumulation of mercury by 3–9-year-old birch trees in all phytomass fractions (20–200 times higher than zonal average values). As a result of this phenomenon, the scales of long-term immobilization of Hg—even with a density of less than 0.02—are 3 times higher than the average level of elimination with harvest in the regional agrocenoses, and reach 80–100 g/km²×year in certain areas with a tree density of 0.8–1.0, which is comparable with the density of the Hg supply from the atmosphere.

Table 4. The ratio of productivity of trees on overgrown abandoned lands to the average increment observed in the zonal forest ecosystems in the central part of Russia

Point	*Species*	*Age, years*	*Tree stand density*	*Soil*	*The ratio of annual increment rates to the average zonal productivity of this species, defined for:*	
					the trunk diameter	*the height*
V	Birch	9	0.015	gray forest medium loamy soil	2.7	1.24
		6	0.115		2.26	1.42
III		15	0.850	sod-podzolic sandy loam soil	0.76	0.92
II	Pine	6	0.503	sod-podzolic sandy soil	2.97	3.25

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Note: the calculations were performed using the database of V.A. Usoltsev (Usoltsev, 2002)

Let us briefly describe the calculation process for the parameter Hg_{BP}^{max} (Figure 8). We used the local site of a former field overgrowing with birch forests with willow inclusions (the average age – 6 years) with a tree stand density of 0.8 (expert assessment), which we had examined, as the basis. The average height of birches in this area turned out to be 540 cm, the diameter at a height of 1.3 m was 5.10 cm; while the standard values for 6-year-old birch forests are 380 and 2.26 cm, respectively (1.4–2.0 times less than the measured values). This is another evidence of high intensity of the growth processes in pioneer communities of woody plants—in those areas of abandoned farmland where they were able to "gain a foothold".

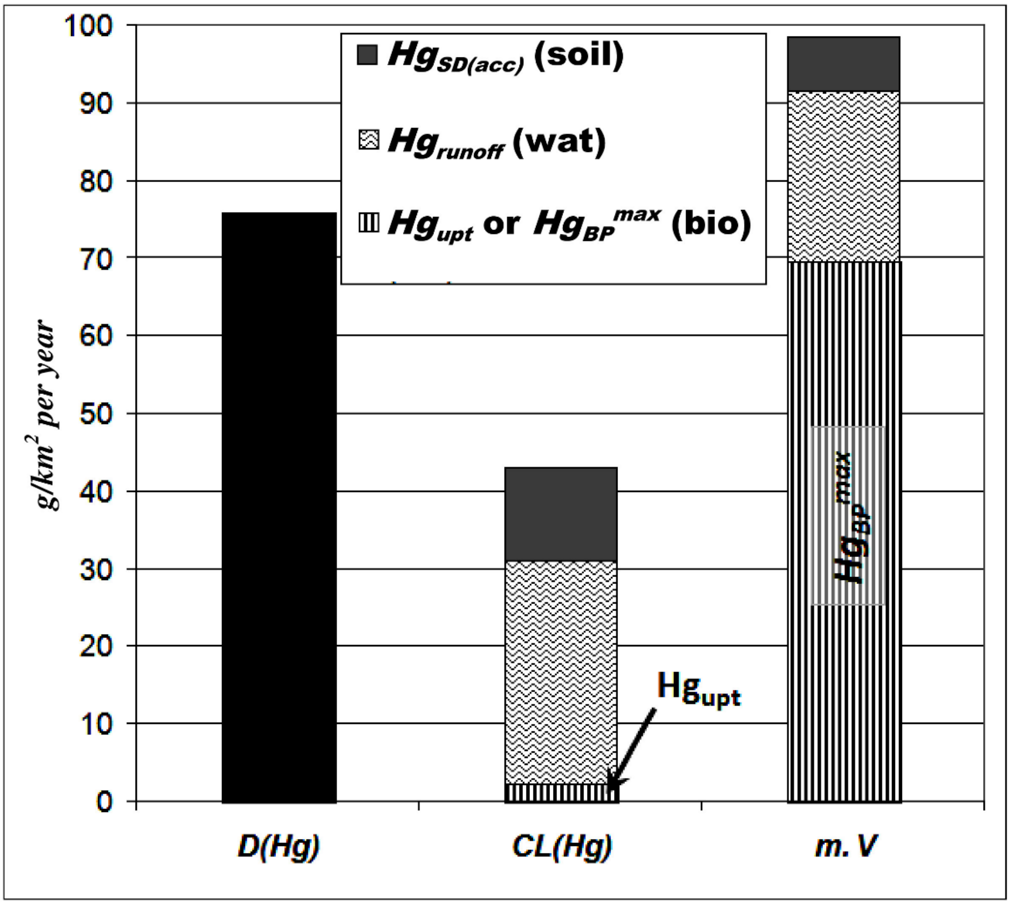

Figure 8. The regional average critical load of mercury ($CL_{(Hg)}$) compared to the average level of its atmospheric deposition in 2010 ($D_{(Hg)}$) and actual bioabsorption at Point V (Hg_{BP}^{max})

Notes. The parameter Hg_{BP}^{max} is just the long-term accumulation of mercury in the incrementing stem wood with bark on the abandoned land in Point V without taking into account recyclable biogenic migration (accumulation in leaves, thin branches, roots, etc.).

The parameter Hg_{upt} is the regional average parameter (determined for biological cycles on lands of all categories with account of the ratios of their sizes) and characterizes the level of annual bioabsorption of Hg, safe for ecosystems and humans. The parameter Hg_{BP}^{max} is the actual Hg bioabsorption by post-agrogenic woody vegetation in Point V, as an example of a possible failure of the landscape bioblock to adapt to technogenesis.

Under these conditions, the reserves of trunk wood with bark of the studied 6-year-old birch forest amounted to 1322.0 t/km^2, and the increase in these phytomass fractions (G_{an} in formula (2)) made 220.2 t/km^2×year (in terms of dry matter with account of the volumetric shrinkage by 12%, average conditional density of 0.568 t/m^3, and tree stand density of 0.8). Knowing that in the total of the indicated fractions of young birch forests, the share of trunk wood is 83%, and that of bark is 17% (its contribution decreases to 10–12% with age), and also taking into account the determined concentrations of Hg in these fractions in Point V (Table 2), we found that 48.8 g/km^2 of Hg is accumulated (removed from the cycle) every year in the incrementing wood, and another 20.7 g/km^2 in the incrementing bark, totaling to 69.5 g/km^2×year of Hg, which is only 8.5% lower than the regional average value of $D_{(Hg)}$.

Analyzing Figure 8, one can wrongly conclude that there is a significant increase in the assimilation potential of the ecosystems in Point V with respect to the anthropogenic supply of Hg. Indeed, the regional average value of $CL_{(Hg)}$ is 1.76 times lower than the density of the technogenic mercury influx from the atmosphere $D_{(Hg)}$, which indicates the redundancy of this influx for the regional landscapes and the growing threat of geochemical equilibrium disturbance (we do not provide the intermediate stages of calculating $CL_{(Hg)}$ and its components in this publication). At the same time, the total contribution of the parameters *bio*, *wat,* and *soil* in Point V—due to the multiple increase in the contribution of the biotic component—completely compensates $D_{(Hg)}$, which can be taken as increasing resistance to Hg influx.

Nevertheless, we consider such an increase in geochemical stability due to land abandonment illusory, because, firstly, it manifests itself at certain spots only (in several abandoned fields with a total area of about 15 km^2), and secondly, it coincides with the path of air migration of emissions from regional center enterprises, and thirdly, it geographically corresponds to the technogenic anomalies of lead, cadmium, and nitrogen in soils, sediments, and natural waters, previously determined by us (Krivtsov et al., 2011). We consider the increase in Hg accumulation by the vegetation of the abandoned lands at Point V to be one of the typical examples of a failure of the regulatory mechanisms of the geochemical cycles of toxicants in the ecosystems under the conditions of technogenic pollution.

Alongside this, birch is the most informative indicator of this phenomenon. In the fundamental monograph by A.L. Kovalevsky (Kovalevsky, 1991), birch was repeatedly mentioned among the species that demonstrate barrier-free or virtually barrier-free absorption of Hg if its bioavailable forms are excessively present in the nutrient medium, and capable of absorbing even gaseous forms of mercury migration.

The abandoned land ecosystems are obviously a "weak spot" with an increased probability of adverse effects of the technogenesis. Indeed, the excess of the CL by the atmospheric supply of the toxicant ($D_{(Hg)} > CL_{(Hg)}$, which is typical for the center of the Ryazan oblast: Figure 8) does not mean any immediate and catastrophic changes in landscapes. This excess only increases the *probability* (risk) of adverse changes: a variety of toxic effects. But there is no doubt that the "weak spots" in this case are the natural-anthropogenic complexes with reduced ecosystem resistance. Abandoned lands are a typical example of such complexes: unlike forest ecosystems and even agrocenoses, they are characterized by a simple structure, poor species variety, predominance of r-strategists (many of which do not have any developed barrier mechanisms of bioabsorption), energy deficiency (lack of contribution from "technogenic energy" in the form of land clearance operations, etc.). The change in the humus content of post-agrogenic soils plays an important role in this case, which is generally aimed at increasing the humus content, but in the first years after the arable land had been abandoned, this process is extremely unstable and in a humid climate, it takes place mainly due to the accumulation of labile organics (Shpedt and Vergeichik, 2014) (a 1.8–5.4-fold increase (Mukina and Shpedt, 2008)). This creates conditions for an increase in the Hg mobility, which has an affinity for organic matter (including due to methylation) and increases the bioavailability of its organomineral forms (Kabata-Pendias and Pendias, 1989; Gordeeva, Belogolova and Andrulaitis, 2012).

All the above prevent the creation of effective mechanisms of geochemical self-regulation ("checks and balances") in spontaneously developing post-agrogenic ecosystems, which could neutralize the effects of impact pollution. As a result, these consequences most clearly manifested themselves in abandoned lands. However, our studies have shown that the

technogenic anomaly of Hg accumulation by woody vegetation in Point V is quite concentrated and does not manifest itself even at a distance of 2–3 km. Thus, it is one of the many examples of the increasingly mosaic pattern of

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the geochemical environment under the influence of anthropogenic impact (Puzachenko, 2004), when a close neighborhood of virtually clean, background areas and small-size, very intensely polluted ecosystems is a typical phenomenon within technogenic aureole (Krivtsov et al., 2011) (Figure 7).

Conclusion

Thus, the spontaneous post-agrogenic degradation of croplands at its early stages is a destructive phenomenon, not only from socioeconomic, but also from ecological and geochemical standpoints. Abandoning arable land reduces the biogeochemical resistance of ecosystems to mercury by up to 35 times. However, under certain conditions, it is the vegetation of abandoned lands that can compensate the supply of Hg from the atmosphere by immobilizing it in trunks and branches due to their less perfect barrier mechanisms of toxicant absorption. Nevertheless, this illusory increase in resistance is in fact an indicator of the failure of the mechanisms of adaptation to technogenic pollution at the ecosystem scale, particularly, if we take into account the effective interception of pollutants migrating in the atmosphere by post-agrogenic communities. Biogeochemical processes in abandoned lands are characterized by extreme irregularity and mosaic pattern of occurrence in space (and, obviously, in time), which is generally typical of the ecosystems that are at the early stages of succession.

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