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DISTRIBUTION AND MIGRATION OF CHEMICAL ELEMENTS IN THE MINOR RIVER BASINS IN THE WEST OF THE SMOLENSK-MOSCOW UPLAND AS AN INDICATOR FOR ASSESSING LANDSCAPE STABILITY

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Hydrological objects link the landscape into connected basins of the paragenetic system through energy and matter migration. It determines the relevance of geochemical monitoring of minor river basins as a condition for designing an effective ecological framework for the territory. We tried to identify regularities of the spatial distribution and migration of chemical elements in the basins of minor rivers in the west of the Smolensk-Moscow Upland. The method of cross-spectrum geochemical analysis helped us to study the river basins of the Vop-Dnieper hydrological region. We compiled 47 complex landscape descriptions. Thus, the maximum calcium and movable magnesium cations values are determined in the super-aqual landscapes of the river basins under study. In the minor river valleys, we find outwash of organic compounds from the outer layers of the geochemical landscape. The research determines the maximum values of the studied elements in the soils of super-aqual landscapes through migration with subsurface and surface run-off. The minimum values are in the eluvial landscape, where there is a partial loss of geochemically movable forms of metals, which increases due to acid and weak-

acid reactions of the environment. Partial outwash of metals, in particular copper and zinc, happens to organic compounds of soils. Trans-eluvial landscape loses trace elements. However, some of them are retained due to falling out of solutions and suspensions. Calculations have shown that copper (conjugation coefficient is 2–3) and zinc (conjugation coefficient is approximately 2) are most actively involved in the migration. In contrast, manganese is less active. The research results present an assessment of the features related to the landscape-geochemical differentiation of the territory of the west of the Smolensk-Moscow Upland from the upper areas of watersheds to the lower elements of landscape-geochemical catenae, including simple drainage basins of minor rivers. The research shows that the active migration of chemical elements characterizes the minor river basins. They are indicators of the geochemical state of the landscape. One can use the research results to assess a landscape-ecological condition, improve an environmental management system, and optimize the natural environment.

Keywords: *minor rivers; ecological framework; migration of elements; geochemical conjugation; elementary landscape*

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РАСПРЕДЕЛЕНИЕ И МИГРАЦИЯ ХИМИЧЕСКИХ ЭЛЕМЕНТОВ В БАССЕЙНАХ МАЛЫХ РЕК НА ЗАПАДЕ СМОЛЕНСКО-МОСКОВСКОЙ ВОЗВЫШЕННОСТИ КАК ПОКАЗАТЕЛЬ ОЦЕНКИ УСТОЙЧИВОСТИ ЛАНДШАФТА

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Гидрологические объекты связывают ландшафт во взаимосвязанные бассейны парагенетической системы посредством миграции энергии и вещества. Это определяет актуальность геохимического мониторинга бассейнов малых рек как условия для создания эффективной экологической структуры территории. Мы предприняли попытку выявить закономерности пространственного распределения и миграции химических элементов в бассейнах малых рек на западе Смоленско-Московской возвышенности. Метод кросс-спектрального геохи-

мического анализа помог нам изучить речные бассейны Вопьско-Днепровского гидрологического региона. Мы составили 47 комплексных описаний ландшафта. Таким образом, максимальные значения катионов кальция и подвижного магния определены в супераквальных ландшафтах исследуемых речных бассейнов. В долинах малых рек мы обнаружили вымывание органических соединений из внешних слоев геохимического ландшафта. В ходе исследования определены максимальные значения изучаемых элементов в почвах супераквальных ландшафтов за счет миграции с подповерхностным и поверхностным стоком. Минимальные значения находятся в элювиальном ландшафте, где наблюдается частичная потеря геохимически подвижных форм металлов, которая увеличивается из-за кислых и слабокислых реакций окружающей среды. Частичное вымывание металлов (в частности меди и цинка) происходит с органическими соединениями почв. Трансэлювиальный ландшафт теряет микроэлементы. Однако некоторые из них сохраняются из-за выпадения растворов и суспензий. Согласно расчетам, медь (коэффициент сопряжения 2–3) и цинк (коэффициент сопряжения около 2) наиболее активно участвуют в миграции; а марганец - наоборот, менее активен. Результаты исследования представляют собой оценку особенностей, связанных с ландшафтно-геохимической дифференциацией территории запада Смоленско-Московской возвышенности от верхних участков водоразделов до нижних элементов ландшафтно-геохимических цепей, включая простые дренажные бассейны малых рек. Исследование показывает, что активная миграция химических элементов характерна для бассейнов малых рек. Они являются индикаторами геохимического состояния ландшафта. Результаты исследования можно применять для оценки ландшафтно-экологического состояния, совершенствования системы природопользования и оптимизации природной среды.

Ключевые слова: *малые реки; экологическая структура; миграция элементов; геохимическое сопряжение; элементарный ландшафт*

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Introduction

In the strategy of achieving sustainable development and functioning of the territory, a special role belongs to the formation of the ecological framework. The essence of this concept lies in the formation of territorial entities

with a special regime of environmental management focused on maintaining an ecological potential in the region. Being a "zone of special environmental responsibility" [4], the components of the ecological framework must ensure the stable development of natural systems. They must stop developing changes and sometimes eliminate deficiencies [1; 7]. Traditionally, the basis of the ecological framework is considered as specially protected natural areas with different environmental management regimes. They are focused primarily on the preservation of the natural landscape. These territories are key areas for monitoring the ecological state of the territory [16]. Experience shows that the current network of special protected natural areas [SPNA] in the regions, including the study area, is still far from optimal. According to geochemical processes, the boundaries of the allocated territories are conditional since the landscape parts form a unitary geochemical system. Hydrological objects (including river basins connecting the landscape into integral paragenetic systems through the migration of energy and matter) are transport corridors of the ecological framework. It determines the relevance of geochemical studies devoted to river basins as an indicator of their transformation and development of approaches for the timely maintenance of background levels. It demonstrates the concentration of chemical elements, which is essential for landscape geochemical stability.

A clear monitoring system to control the transit of chemicals in the elements of the ecological framework does not exist yet.

A.V. Khoroshev's works include geochemical aspects related to the design of the ecological framework through establishing spatial distribution patterns and migration of chemical elements in the agrarian landscape of the taiga zone. It has been established that "at certain spatial ratios of the catena parts and a certain critical width of the buffer strip, the polluting effect of lateral flows of substances from arable land ceases to manifest itself in the accumulative catena parts" [17].

The researchers have been actively developing the issue regarding the geochemical indication of the marsh landscape transformation. According to the research, the content of elements in marsh ecosystems different in the genesis of peat sediments and different regions allows one to predict the geochemical situation in the territory under study [5].

A subject of interest is the influence of various natural and anthropogenic factors on the activity of elements, and the intensity of lateral and radial migration of matter, the genesis and role of landscape-geochemical barriers in maintaining ecological balance [9]. The content of mobile forms of microelements in alluvial soils of floodplains is considered an indicator of chemical pollution in water protection

zones of small rivers [2; 8; 9; 11; 13; 15; 19; 20; 21; 25]. Particular attention in research is paid to the migration and accumulation of heavy metals [22–24].

Basin landscape geochemical analysis is one of the actively developing areas of landscape and geochemical research. At the regional level, the objects of landscape and geochemical studies, as a rule, are different river basins. Basin, soil, and biogeochemical paragenetic associations of landscapes are investigated for accumulation or depletion of chemical elements, and the presence of correlations [6; 14]. The studies give preference to analyzing the geochemical characteristics of the waters and bottom sediments of minor rivers as indicators of their ecological state and a source of mineral resources [12; 20].

We should identify the landscape features and geochemical differentiation of minor river basins and the regularities of the spatial distribution and migration of chemical elements in the subordinate landscapes.

The study investigates a hypothesis that the minor river basins in the west of the Smolensk-Moscow Upland are linear elements of the ecological framework. The active migration of chemical elements characterizes them. They can be indicators of the landscape's geochemical state.

The paper deals with conjugated elementary landscape parts as cascade systems with unidirectional matter streams in the west of the Smolensk-Moscow Upland characterized by a developed system of minor rivers. The basins of these objects are the least explored in geochemical terms; they are very vulnerable to external influences by water bodies.

The paper aims to identify patterns of spatial distribution and migration of chemical elements in the subordinate landscape.

Materials and methods

The systematic approach is a methodological basis for solving the study objectives. The study applies methods of complex physical-geographical research, comparative-geographical, landscape-geochemical, and analytical methods. The cross-spectrum geochemical analysis is used as the leading method for studying the complex of minor river valleys [3].

We obtained materials during complex field landscape research of the minor river valleys of Dukhovshchinskaya Upland and the Smolensk-Krasninskaya Upland. They belong to the western part of the Smolensk-Moscow Upland and the Vop-Dnieper hydrological region. We have selected typical minor rivers for our study: the Tsarevich, the Krupitsa, the Maly Vopets, and the Zalaznya (within Dukhovshchinskaya Upland), the Ufinya and the Dobraya rivers draining the Smolensk-Krasninskaya Upland. The areas of the studied valleys be-

long to either natural or natural and anthropogenic landscapes. Near the river basins of the Tsarevich, the Maly Vopets, the Zalaznya, and the Dobraya, an autonomous landscape is formed on flat watersheds serving as sediment with partial small-leaved forests. Natural landscapes formed under the typical coniferous-broad-leaved and small-leaved forests coincide with the studied areas of the Ufinya and Krupitsa river basins. In the studied areas, the ravines, as a rule, do not go far in the interfluves associated with dense moraine sediment restraining the linear surface erosion [18]. The watersheds are most often covered with loessoid sediment. In general, the minor rivervalleys significantly enhance the contrast of the relief; they form a geochemical landscape typical for the region.

The research studied the water bodies in the upper and middle streams. Within the study area, we have presented 47 complex landscape descriptions from 2003 to 2018.

Field catena in the minor river valleys covers conjugated elementary landscape making paragenetic systems with one-way vectors of matter motion. Soil pits are laid in autonomous (eluvial), trans-eluvial, trans-accumulative, and super-aqual landscapes. Thus, we conducted soil sampling.

The studies involved certified methods. The acidity of the water and salt soil extracts is determined by the potentiometric method. The Kappen method assists in identifying hydrolytic acidity. The bichromate method modified by I. V. Tyurin is used to find soil organic matter. The number of absorbed layers is determined by the accelerated Kappen-Golkovits method. The method of flame atomic absorption spectrometry based on an atomic absorption spectrometer, "Spectrum – 5" allows establishing the content of geochemically base forms of metals (Mn, Zn, Cu, Pb).

The results are processed according to analytical and graphical methods. To assess the intensity of migration of chemical elements in the catenae, we use the coefficient of lateral differentiation K_L.

Results

The geochemical character of the matter and energy migration in the basins of minor rivers is observed as a change in chemical properties from the upper sections of the watersheds to the lower elements. Fig. 1 demonstrates changes in the actual acidity in the elementary landscape of river valleys. Studies have shown that for the humus horizons of the elementary landscape, pH changes from acidic to neutral values (4.8–6.8).

The type of vegetation determines actual soil acidity in the eluvial landscape in the river basins under study. Thus, an acidic environment is determined in the

soils formed under coniferous and deciduous forests (basins of the Krupitsa and Ufinya rivers) (4.8 and 5.1, respectively). The eluvial parts of the geochemical landscape formed under the deposits in the river basins have a weakly acidic and neutral reaction. It indicates a residual effect of human agro-economic activity on their chemical properties.

Trans-eluvial landscapes are characterized by noticeable soil acidification on the upper slopes of river valleys (pH is from 4.1 to 5.9), which is most likely due to the active outwash of soluble forms of salts from the humus horizon along with surface run-off.

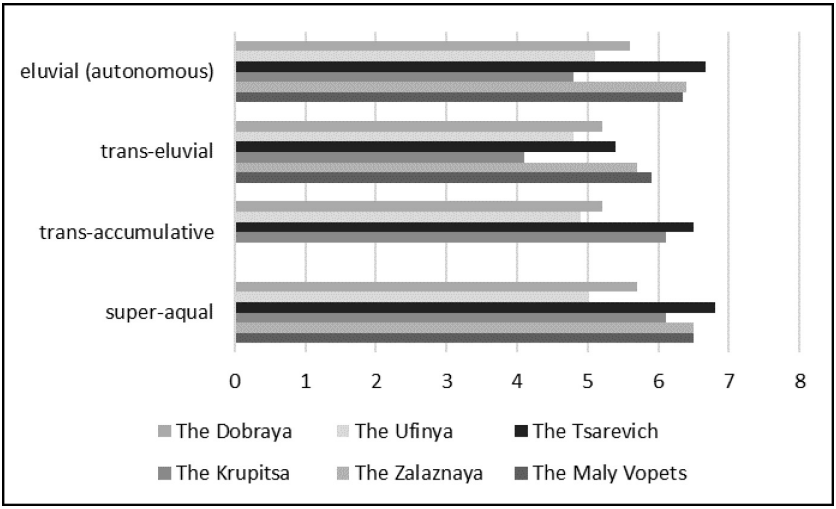

Fig. 1. Distribution of soil acidity of minor river basins in the west of the Smolensk-Moscow Upland.

We observe partial accumulation of salts in the lower parts of the geochemical landscape (trans-eluvial and super-aqual landscapes), where weakly acidic and neutral reactions of the environment have already been starting to prevail.

The migration processes and accumulation of elements in the parts of the geochemical landscape are clearly visible due to the analysis related to the distribution indicating the sum of absorbed bases in the soils of minor river basins (Fig. 2). The studies showed that the maximum calcium and magnesium movable cations values are determined in the super-aqual landscapes of all river valleys (from 10 to 17.5 mg-eq / 100 g of soil). We can see an intensive

outwash of elements from eluvial and trans-eluvial elementary landscapes. The maximum values of outwash are indicated in the soils of the Maly Vopets and Zalaznya river basins, within which trans-eluvial landscapes occupy the steep upper slopes of the valleys.

The minimum values demonstrating the sum of absorbed bases are seen for the Krupitsa valley, where the soil-forming material of the eluvial and trans-eluvial parts of the geochemical landscape has a lighter granulometric composition.

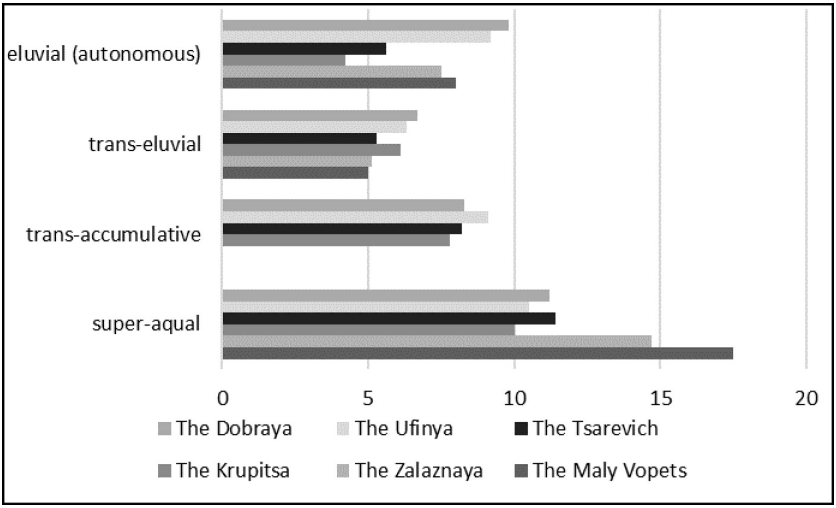

Fig. 2. The distribution shows the sum of absorbed bases in the soils of minor river basins west of the Smolensk-Moscow Upland (mg-eq/100 g of soil).

In the minor river valleys, we observe the outwash of organic compounds from the outer layers of the geochemical landscape. Fig. 3 shows the results of the analysis of the humus content in the soils under study.

The largest outwash of organic matter happens to river valleys with steep slopes, where washed-off and highly eroded soils are formed in the trans-eluvial landscapes. In some cases, the humus content can drop to 0.88%–1.3%. At the same time, there is a noticeable accumulation of organic matter in super-aqua-land trans-accumulative landscapes. The chemical properties of soils affect the activity of elements, especially geochemically movable forms of metals. Table 1 presents the content of Cu, Zn, Pb, Mn in the basins of the Maly Vopets and Krupitsa rivers.

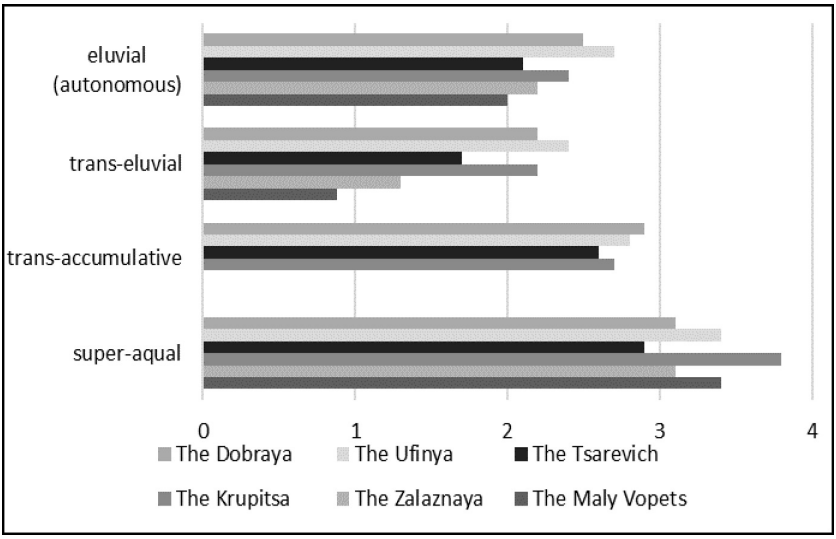

Fig. 3. Distribution of humus in the soils of minor river basins in the west of theSmolensk-Moscow Upland (%)

Table 1.

Geochemically movable forms of disseminated metals in soils of elementary landscapes of river valleys

Elementary landscape	Metals, mg/kg			
	Mn	Cu	Zn	Pb
The MalyVopets river				
Eluvial	71	2.91	13.66	6.34
Trans-eluvial	85.38	3.05	17.33	6.68
Super-aqual	86.1	8.96	29.09	7.5
The Krupitsa river				
Eluvial	70.98	2.04	9.56	3.33
Trans-eluvial	77.21	4.5	15.01	5.1
Trans-accumulative	90.35	2.78	12.62	4.46
Super-aqual	80.6	4.09	19.51	5.89

Among the disseminated metals in the elementary landscapes under study, the highest concentration is distinguished by manganese, which amounts from 71 to 90 mg/kg in the soils under study. Lead is the least of all elements in the soils of the river valleys. Its concentration is from 3.3 to 6.7 mg/kg.

The research determines the maximum values of all studied elements in the soils of super-aqual landscapes due to migration with subsurface and surface run-off. The minimum values are noted in the eluvial landscape, where there is a partial loss of geochemically movable forms of metals, which increases due to acid and weak-acid reactions of the environment. Partial outwash of metals also happens to organic compounds of soils, particularly to copper and zinc. Trans-eluvial landscapes mostly lose trace elements. However, some of them retain, and they fall out of solutions and suspensions.

The metal mobility in the parts of the geochemical landscape makes it possible to estimate the coefficient of lateral differentiation (K_L). The results of calculating K_L for all elements are presented in Fig. 4. Calculations showed that copper is most actively involved in migration; its coefficient is 2–3. Zinc has a rate of about 2. In contrast, manganese is less active. At the same time, manganese, copper, and zinc more actively migrate and accumulate in the valley of the MalyVopetsin, a stronger dissection of the relief.

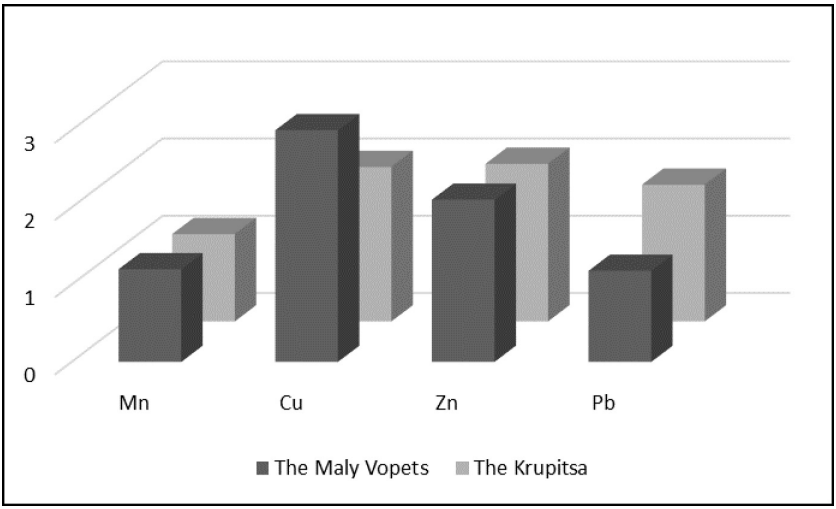

Fig. 4. Coefficients of lateral differentiation of metals in the valleys of the Maly Vopets and Krupitsa rivers

Geochemical studies prove that there is an active transfer of matter and energy in the minor river valleys. Any geochemical transformations, including those associated with human activities, affect the chemical composition of subordinate landscapes. One can use the results as reference sites for mon-

itoring studies and control over the state of natural, natural, and anthropogenic landscapes.

Discussion

The previous studies related to this area included some geochemical aspects. In particular, the studies have found that iron is less involved in biogenic migration than manganese, but rather intensively migrates with surface and subsurface water flows. Iron with hydrogen is a typomorphic element for conjugated landscapes[3].

The chemical condition of the region's flood plain soils has been studied according to the assessment of their fertility and use [10]. The design of the landscape-ecological framework of the region is based on a constructive landscape-geographical approach. The published works emphasize areal elements of the ecological framework [18].

The research novelty is emphasized by its subject, including features of the spatial distribution and migration of chemical elements in the basins of minor rivers in the west of the Smolensk-Moscow Upland. The results complement and expand the understanding of the dynamics, interrelationships, and direction of the development of landscapes in the minor river basins. They present a complete picture of geochemical transformation.

Nevertheless, the results only underline the possibility of including minor river basins in the ecological framework monitoring programs. The results relate to certain indicators of geochemical changes. Undoubtedly, the problem concerning the observation of the geochemical stability of geosystems in the minor river basins requires the expansion of the analyzed geochemical aspects and determination of optimal indicators marking changes in the landscape.

Conclusion

We tried to assess the features of the landscape-geochemical differentiation of the territory from the upper sections of watersheds to the lower elements of landscape-geochemical catenae, including simple drainage basins of minor rivers in the west of the Smolensk-Moscow Upland. Geochemical studies have led to the following conclusions. The chemical properties of the accumulative horizons of soils in autonomous and trans-eluvial landscapes are mainly characterized by an acidic environment, which affects the increase in metal mobility. The change in the accumulative parts in the acid landscape to neutral values contributes to their accumulation. The studied catenae present an intensive outwash of calcium and movable magnesium cations from the upper parts of the

geochemical landscape and subsequent accumulation in super-aqual landscapes (from 10 to 17.5mg-eq/100 g of soil). The outwash of organic compounds is also noticeable, where washed-off and highly eroded soils are formed under the conditions of trans-eluvial landscapes. The study area shows an active outwash of zinc and copper in the upper elementary landscapes. These elements intensively accumulate in the super-aqual elementary landscapes. At the same time, manganese, copper, and zinc migrate more actively and accumulate under a stronger dissection of the relief. Transformation, including anthropogenic, eluvial, and trans-eluvial landscapes of minor river basins, on the one hand, contributes to a change in the pH value towards a neutral reaction, reducing the metal mobility. On the other hand, it stimulates the planar washout of soil organic matter on non-sodded slopes.

The revealed patterns confirm the assumption that the active migration of chemical elements characterizes the minor river basins in the west of the Smolensk-Moscow Upland. Therefore, the dynamics of geochemical processes are an indicator of the landscape condition. It can be considered a component included in the system of indicators for assessing the overall stability of landscapes.

We believe that geochemical monitoring of the accumulating part of the geochemical landscape without additional complex studies of the entire basin makes it possible to obtain the necessary geochemical information on the territory's stability within the entire paragenetic system.

In the future, the study results will be in demand for the design of the ecological framework of the territory under study. They may form the basis for the development of a program aimed at monitoring its condition.

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