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Material Composition and Geochemical Characteristics of Technogenic River Silts

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Abstract—The paper discusses the results of many years of studying the material composition and geochemical characteristics, conditions, and processes in the formation of technogenic river silts: a new type of modern river sediments formed in riverbeds within the boundaries and zones of influence of industrial–urbanized areas. The article examines the main sources and most important characteristics of technogenic sedimentary material flowing into rivers, as well as the geochemical conditions of technogenic alluvial sedimentation, the morphology and structure of technogenic silts, the extent of their spatial distribution in riverbeds, their grain size characteristics, and mineral and chemical composition. Special attention is paid to analyzing the group composition of organic matter in river sediments and the features of its transformation in pollution zones. The study analyzes the technogenic geochemical associations that form in silts in zones of influence of various impact sources, the features of the concentration and distribution of chemical elements, heavy metal speciation, the composition of exchangeable cations in technogenic silts and natural (background) alluvium, and the composition of silt water. Possible secondary transformations of technogenic silts and their significance as a long-term source of pollution of the water mass and hydrobionts are substantiated.

Keywords: alluvium, sedimentary material, river, river channel, technogenic silt, city, pollution source, geochemistry, material composition, chemical elements, heavy metals, speciation, geochemical anomaly

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INTRODUCTION

Sedimentogenesis, i.e., the formation of loose sediments, is rightly regarded as the most important process in the natural dynamics of the Earth's surface. It is manifested on the entire surface of our planet and in fact is a global geochemical process associated with differentiation of sedimentary material and migration of chemical elements. The characteristics of the end products of sedimentogenesis largely depend on the input sources, the material composition of the material involved in sedimentation, and the geochemical conditions of the sedimentation setting. In the general sedimentogenesis scheme, two successive stages are distinguished: (1) catchment-area (slope–valley–delta) and (2) basin sedimentogenesis (Strakhov, 1983). One of the products that forms at the first stage is alluvium, i.e., sediments that accumulate in river channels and valleys and the floodplains and terraces making them up.

Under natural conditions, the formation of alluvium is controlled by the nature and intensity of erosion and removal of soil and rock and the transport and deposition of sedimentary material by watercourses, all of which act as an erosion–accumulation complex (Makkaveev and Chalov, 1986). The geological structure and vegetative–soil cover of catchment areas create the general background that predetermines the lithological, mineralogical, and geochemical characteristics of alluvial sediments. The end result of the concomitant impact of these processes, manifested in the accumulation of alluvium, also depends on the hydrological regime of watercourses, which in turn is governed by the interacting factors that directly or indirectly influence river runoff. Mechanical differentiation and fractionation of solid phases, the physicochemical parameters of the alluvial sedimentation setting, and processes that determine the behavior of chemical elements in the water column and bottom sediments, as well as seasonal changes in the hydrological regime of the river, water flow hydraulics, and the degree of saturation of its sedimentary material—all of these are particularly important for the material composition of alluvium and its subsequent transformation. Usually, under natural conditions, there is a certain sedimentary material balance in catchment area–riverbed and erosion–transport–accumulation systems.

In industrial–urbanized areas (in technogenic landscapes), considerable masses of material are involved in alluvial sedimentogenesis, the occurrence of which in the sedimentary cycle is related to human economic activity and is characterized by a specific material composition and high concentrations of

Fig. 1. Sketch map of Moscow region (not to scale): I, background area; II, Pakhra River basin.

many chemical elements and compounds (Yanin, 2002a, 2007b, 2018). This ultimately disrupts the above-mentioned sedimentary material balance and leads to the formation of a new type of sediment in riverbeds: technogenic silts, which differ from natural channel alluvium in morphological appearance, material composition, physicochemical properties, and geochemical characteristics (Yanin, 1994, 2013a, 2018). In most cases, it is the intensity and scale of technogenic alluvial sedimentation, the main material product of which is technogenic silts, that determine the most important ecological and geochemical features of rivers in developed areas.

The proposed work is based on materials and data obtained by the author in 1978–2018 in different regions of the former Soviet Union and contemporary Russia while carrying out scientific and applied hydrochemical, ecological, and geochemical studies, as well as scientific and problem-oriented prospecting, engineering, and environmental surveys. The article considers the main sources and the most important characteristics of technogenic sedimentary material flowing into rivers, as well as the geochemical conditions of technogenic alluvial sedimentation, the morphology and structure of technogenic silts, the extent of their spatial distribution in river channels, the grain size characteristics, and mineral and chemical composition. Special attention is paid to analyzing the group composition of organic matter in river sediments and the features of its transformation in pollution zones. The study analyzes the technogenic geochemical associations that form in silts in zones of influence of various impact sources, the features of the concentration and distribution of chemical elements, heavy metal speciation, the composition of exchangeable cations in technogenic silts and natural alluvium, and the composition of silt water. Possible secondary transformations of technogenic silts and their significance as a long-term source of pollution of the water mass and hydrobionts are substantiated.

The author is grateful to his teacher, doctor of geology–mineralogy Yu.E. Saet (1934–1988), at whose initiative and under whose leadership studies of the processes and products of technogenic alluvial sedimentogenesis were begun in 1978. The author is particularly grateful to Academician E.M. Galimov for valuable comments and friendly support in preparing the work for publication.

BRIEF DESCRIPTION OF THE MAIN AREAS AND RESEARCH METHODS

Expeditionary studies, the results of which form the basis of this work, were carried out in different years within Moscow oblast (Moscow region), the Republic of Mordovia (Mordovia region), and central Kazakhstan (Kazakhstan region). These regions are characterized, on the one hand, by a high degree of economic development, and on the other, their borders contain territories not directly affected by technogenesis. This made it possible to obtain material reflecting the different intensities of technogenic impact on water systems and study a number of situations unique from the ecological and geochemical aspect, largely due to active technogenic alluvial sedimentation.

Within the Moscow region, field studies were carried out in the Pakhra River basin (the Pakhra proper and nearly all of its tributaries), on rivers (Moscow, Klyazma, Vokhonka, Lavrovka, Lama, Vyaz, Protva, Osyotr, Sestra, Istra, etc.), and large streams in the zones of influence of various cities and towns (Moscow, Shchelkovo, Noginsk, Elektrostal, Obukhovo, Kolomna, Dmitrov, Voskresensk, Volokolamsk, Vereya, Khorlovo, Zaraysk, Lotoshino, Katuar, Karasevo, Klin, etc.), and on lakes (Glubokoe, Senezhskoe, Kosinskoe) (Fig. 1). The most detailed studies were carried out within the typical small Pakhra River basin, a right tributary of the Moscow River (Resursy..., 1973a). The length of the Pakhra is 135 km, and the catchment area is 2720 km^2.

The materials of the geological survey indicate that the rocks that have the main influence on local landscapes are characterized by relative depletion of the mineral composition and the content of most chemical elements within their global distribution parameters in the lithosphere and sedimentary rocks. The main type of relief in interfluvial spaces is loamy moraine plain, dissected by an erosion network of gullies and ravines. Up to 50% of the Pakhra catchment area is covered with mixed forests on soddy-podzolic soil.

The hydrological regime and water content of the Pakhra, which is attributed to Eastern European–type

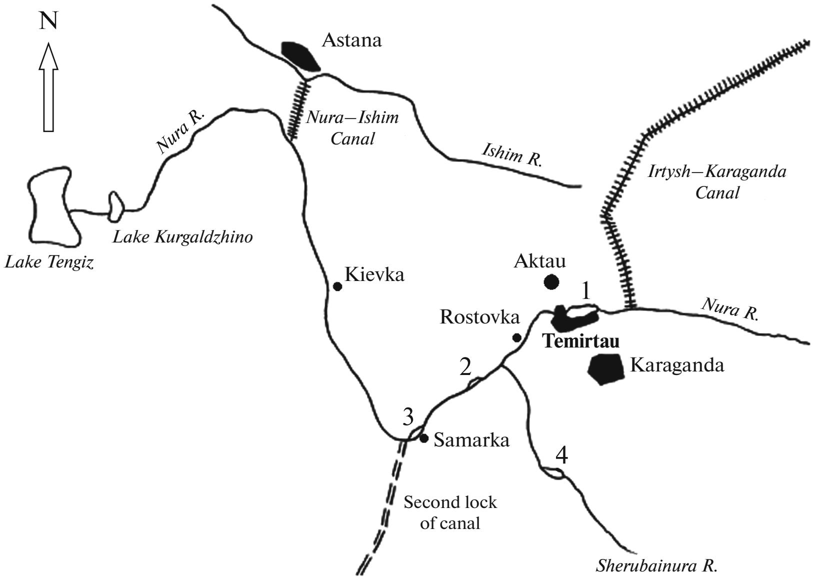

Fig. 2. Sketch map of Nura River basin (Kazakhstan region, not to scale). Reservoirs: (1) Samarkand; (2) Intumak; (3) Samara; (4) Sherubainura.

rivers mainly fed by snowmelt, are common and normal for the small rivers of central Russia. The average annual discharge below Podolsk is 9.95 m^3/s, the annual runoff modulus is 5.65 L s km^{-2}, and the solid runoff modulus is 5–30 t km^{-2} yr^{-1}. In the spring, flooding accounts for 40 to 75% of aqueous runoff. Winter runoff is constant and usually accounts for less than 10% of the annual runoff. Summer–autumn runoff is relatively diverse and in some rainy years reaches the dimensions of spring flooding. In recent decades, wastewater from industrial facilities, cities, and towns (usually via streams and small watercourses) has played an important role in the Pakhra's water supply. A particularly significant amount of wastewater flowed into the Pakhra near Podolsk, a city that during the research period hosted large food processing enterprises and battery, mechanical, electromechanical, cable, chemical–metallurgical, microwire, construction-material, nonferrous-metal, and other types of plants. The main discharge of industrial and domestic wastewater occurs from the city's treatment plant along Cherny Creek. A small amount of wastewater entered the Pakhra via a system of small streams from above and below Cherny Creek. Below Podolsk, the Shcherbinsky landfill was located on the right bank of the Pakhra (which has since been reclaimed), which was drained by the Konopelka River and (before reclamation) small streams.

Within the Kazakhstan region, the bulk of research was carried out in the Nura basin—the largest river of the small Kazakh mountains, which flows into the Tengiz–Kurgaldzhin lake system (Spravochnik..., 1933). The Nura is 911 km long, and the catchment area is 58100 km^2. The river basin is located in the steppe zone; the climate here is sharply continental arid, and the annual rainfall is 300–350 mm, which is almost completely evaporated. The Nura enters the complex water management system of central Kazakhstan, the main core of which is the Irtysh–Karaganda canal, which has operated since 1974 (Fig. 2). The Sherubainura is the Nura's main tributary (278 km in length).

In terms of landscape, a large part of the Nura basin is located in the subzone of arid steppes on dark chestnut soils; in some places, there are forb-grass steppes on southern black soils and solonetzic and meadow-chestnut soils; a zone of light-chestnut soils begins in the southern regions (Sherubainura basin) The western part of the basin (the Tengiz-Kurgaldzhin depression) pertains to the semiarid zone with dark chestnut solonetzic soils. The Nura delivers water to Lake Kurgaldzhin and (only in very high-water years) to the bitter Lake Tengiz, which lies at the bottom of a large inland depression made up of gypsum-bearing rocks. The Kurgaldzhin nature reserve is a unique wetland for migratory birds (including rare) wintering in southern countries.

In its upper reaches, the Nura is a small, shallow, steppe river with an abundance of bars, although it floods heavily during the high-water season. After the confluence of the Irtysh–Karaganda canal (below the Samarkand Reservoir), the watercourse is quite abundant for such areas, often with a swift current. The river channel is 35–45 m wide, sometimes up to 80–100 m; the channel depth in some areas reaches 5–6 m or more, and the most common maximum depths are 2.5–3 m. Submerged landforms and islands are widespread on the river, there are numerous oxbows, and in some places, the channel strongly meanders. In its

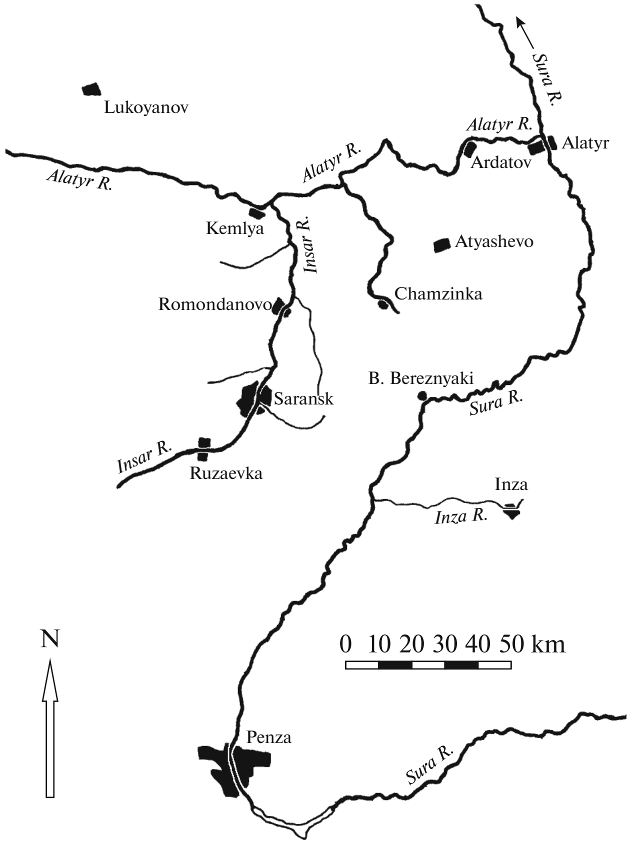

Fig. 3. Sketch map of Mordovia region.

hydrology, the Nura pertains to Kazakhstan steppe rivers; maximum flow is observed in spring and lasts 3–4 weeks. The typical monthly average flow rate (below Temirtau) during winter low water is 6–10 m^3/s; this may increase sharply during the spring flood: 17–129 m^3/s; in summer, it is 4–7 m^3/s. Salinity varies from 200 to 1200 mg/L; sodium predominates among the main ions, the chloride and sulfate contents increase during low water, and hydrocarbonates and calcium increase during high water. Solid runoff increases downriver, with increased turbidity (usually in the range of 10–40 mg/L) associated with increased water flow.

In 1986, construction began on the second stage of the Irtysh–Karaganda canal, from the Nura and farther to areas of Dzhezkazgan (Karaganda–Dzhezkazgan canal). In accordance with the project, an approximately 110-km-long segment of the Nura channel from Temirtau to Samarka) was proposed for use as a natural route connecting both channels, but this particular segment demonstrated an extremely high level of mercury contamination, most of which was concentrated in channel sediments (in technogenic silts). For a long time, mercury was used in significant quantities as a catalyst in the production of acetaldehyde at the Carbide Plant in Temirtau (Yanin, 1989, 1992). Until 1976, mercury production at the plant operated without local treatment facilities, which left mercury to be carried away in runoff. In 1976, local wastewater treatment plants were put into operation, after which sewage, together with general plant wastewater, went to a city wastewater treatment plant, where it was subjected to additional biochemical treatment. Wastewater discharge from treatment plants occurred in a steady-state mode, up to 20% of the low-flow rate of the Nura in volume. For the plant's annual mercury use of about 70 t, up to 54–55 t of it passed into mercury-bearing sludge, while the remainder was irretrievably lost (mechanical losses along with wastewater passed into sewage sludge, etc.). It is estimated that during the entire period of acetaldehyde production, up to 500 t of mercury in wastewater entered the Nura, about 150 t of mercury was emitted into the atmosphere, about 250 t was accumulated in homogenization field sludges (at sewage treatment plants), up to 100–150 t (possibly more) ended up at a sludge storage plant, and up to 300 t were contained in sewage sludge. In total, this is at least 1300 t of gross irretrievable mercury loss. In addition, the Nura received wastewater from a large metallurgical combine (LMC) and a coal-fired power plant (SDPP-1) in Temirtau. The Nura even received the direct discharge of slurry waters from SDPP-1, which contained up to 2500 mg/L of SPM (coal ash, the discharge of which into the river is estimated at several million tons). In the village of Aktau, there is a large cement plant. Additional technogenic load on the Nura basin is associated with certain other enterprises in this industrial district.

In the Mordovia region, the bulk of research was carried out on the Insar, Alatyr, and Sura rivers (Fig. 3). The Insar is 168 km long, its basin area is 4020 km^2, and the long-term average water discharge near Saransk is 6 m^3/s (Resursy..., 1973b). The Insar is a typical lowland river, the channel and flow of which are formed in the forest–steppe zone. The river is fed mainly by snowmelt, as well as by a certain volume of ground- and rainwater; in recent years, this has been augmented by industrial and domestic wastewater, whose share in average annual water runoff reached 20–25% by the early 1990s. Within the basin, adjacent to the riverbed, leached and podzolic chernozems are widespread; in some places (in the upper reaches), gray and dark gray forest soils occur; in the lower reaches, alluvial soils. A significant part of the floodplain is under plow.

The bulk of wastewater was discharged into the Insar from the Saransk city treatment plants (CTPs) on the left bank of the river (northern outskirts of the city). Wastewater also flowed into the river from local industrial wastewater treatment plants (LTPs) along the Lepeleyka River (southern industrial zone: medical equipment, electronics, and beverage plants) and along Nikitinsky Creek (wastewater from the central industrial zone: cable, electric, mechanical, instrument, medical, dumptruck, and other types of factories).

In the city of Saransk (with an area of 70 km^2) and its industrial suburbs is a segment of the Insar from its confluence with the Lepeleyka River (southern border of the city, 55 km from the source of the Insar) to the transect of the CTP (northern border of the city, 75 km from the source). Geomorphologically, the Insar riverbed in and below Saransk is characterized by favorable sediment accumulation conditions. Seventy-five kilometers below the CTP, the Insar flows into the Alatyr River (a left tributary of the Sura, in the Volga Basin). The Alatyr is 296 km long, the area of the basin is 11200 km^2, and the average annual flow rate near the main observation site (70 km below the mouth of the Insar) is 40 m^3/s. The maximum flow occurs during the spring flood, and the minimum, in the winter. Approximately 25% of the Alatyr's water runoff comes from the Insar. The Sura River, a right tributary of the Volga, is 841 km long, and the area of the basin is 67500 km^2.

The general principles of geochemical environmental research are discussed in (Saet et al., 1990; Yanin, 1999). The geochemical research methods for the processes and impact of technogenic pollution of water systems are detailed in (Saet et al., 1982; Saet and Yanin, 1985; Yanin, 2002b). At all river areas, geochemical mapping of bottom sediments was carried out (an en route survey was commonly used with a sampling step of 250 m). In order to establish technogenic geochemical associations peculiar to different pollution sources, bottom sediments were sampled at a step of 10–20 m in their zones of influence. To obtain relatively reliable characteristics for technogenic geochemical associations, at least 30 samples were taken for each sampling set. Areal surveys of the channel were organized at characteristic sectors of the rivers with a sampling step of 2–5 m.

Channel sediments (alluvium, silt) were retrieved with a plastic scoop at insignificant channel depths or with a TBG-1 borer at significant depths. Sewage sludge and industrial slurries were sampled with the TBG-1 corer at the place of their localization (silt and sludge maps); samples from the upper soil horizon were taken with a plastic shovel; from soil pits, with a soil knife. The mass of the material collected into each main sample (in white cotton bags) was no less than 300 g. Samples of sediments and other sedimentary formations were pretreated for analytical studies according to known methods (Saet et al., 1982, 1990). The samples were air-dried in shade under well-ventilated conditions with periodic (three to four times a day) crumbling of each sample. They were then run through a capron or duralumin sieve with a mesh size of 1 mm, quartered, and placed in tracing-paper bags; control duplicates were placed in Kraft paper bags. Samples from the same set were packed in a plastic bag to reduce the likelihood of secondary contamination during storage and transport. Samples were pretreated for further analytical studies as quickly as possible. During preparation for analyses, bottom sediment samples meant for testing mercury distribution were only sieved (i.e., they were not pulverized). "Fresh" sediment samples for particle size and chemical element speciation analysis were placed in plastic containers. Samples of bottom sediments for isolation of silt water (by centrifugation) were collected in white plastic buckets. In all cases, the given material was morphologically described directly at the sampling site. In order to obtain significant charges of river SPM, water samples 120–160 L in volume were left to settle for 24 h in white polyethylene tanks, then the water was siphoned off; the precipitate (i.e., SPM) was dried in air and placed in glass weighing bottles. Later, this separation SPM was used for silicate analysis and determination of a wide range of chemical elements and metal species in it.

On the Nura River, in addition to standard en route testing, the so-called method of transect-based testing of technogenic silts was applied. Its essence is as follows. A hydrological profile (transect) was laid across the river channel, on which depth measurements were taken (every 1 m along the profile). At the same time, the lithology of bottom sediments beneath the riverbed was described. Then, the TBG-1 borer was used from a launch (moving along a marked cable strung across the channel, which made it possible to clearly fix the sampling point on the transect) to recover bottom sediments on so-called sampling verticals. The number of the latter was determined by the width, lithological structure, and flow hydrodynamics of the channel. Silt was sampled on each vertical, as a rule, along the 0–20 cm, 20–40 cm, etc., horizons to the source alluvium, which was also tested. Samples of channel alluvium (varieties of sands) were taken from the upper layer (up to 20–30 cm thick). Near each transect (up to 100 m up- and downstream), technogenic silts were additionally sampled in characteristic areas of the channel (frequently to the full thickness of the latter). Backwaters, point bars, sand banks, and areas of high aquatic plant growth were thoroughly sampled, i.e., places where silt accumulation was expected. Such testing makes it possible to reveal the three-dimensional structure of pollution zones recorded by riverbed deposits, to virtually eliminate the probability of error that occurs when taking a single sample at the waterline, and to objectively assess the extent of technogenic sedimentation and, accordingly, the level of river pollution. In 1986, 34 such transects were laid on a segment of the Nura River stretching ~105 km from the Samarkand Reservoir to the village of Samarka. In 1997, in the first 25 km from the Samarkand Reservoir, sampling transects were placed at steps of 250 m, then (up to the headwaters of the Intumak Reservoir), every 1 km; The total length of the segment was about 80 km, encompassing 156 transects.

The transect-based silt testing method was also used in chosen segments of the Insar, Alatyr, and Sura rivers.

Within each region, in order to obtain information about the material composition and geochemical features of the background channel alluvium, areas of the hydrological network not subjected to direct technogenic impact were studied (sampled) (Yanin, 2002b, 2011).

Samples of alluvium, technogenic silts, sewage sludge, sludges, separation SPM, and soils were studied analytically by the following methods. Gross concentrations of Cr, Mn, Co, Ni, Cu, Zn, Mo, Ag, Cd, Pb, and Bi were determined by atomic absorption; Hg, by flameless atomic absorption; Rb, Sr, by flame photometry; Th, U, by X-ray spectroscopy; Se, by fluorimetry; Tl, by extraction photometry; B, F, Ti, V, Ge, As, Zr, Sn, Sb, Ba, and W, by quantitative emission spectroscopy; Li, Be, P, Sc, Ga, Sr, Y, Nb, La, and Yb, by approximate quantitative emission spectroscopy. For the control, 20% of the samples (in each sampling) were studied by group quantitative emission spectroscopy for 17 elements; 10% of samples were studied by the atomic absorption method (Cr, Co, Ni, Cu, Zn, Cd, Pb). The petrochemical components of sediments were determined by gravimetric, volumetric chelatometric, potentiometric, flame-photometric, and photocolorimetric methods. The particle size analysis of the sediments was carried out by the water–sieve method: the >0.25 mm fractions were removed with a sieve; smaller particles, by elutriation and pipetting. The chemical element distribution in the particle size fractions was studied by atomic absorption and quantitative spectroscopy. To determine metal speciation in sediments (sewage sludge, slurries, alluvium, silts, river SPM), different variants of phase analysis were used (sequential, selective extract) (Razenkova et al., 1984; Saet, Nesvizhskaya, 1974; Saet et al., 1990). The test results are given per dry weight of the sample.

A set of hydrochemical studies was also performed at all sites, aimed at investigating the chemical composition of surface, ground-, drinking, and irrigation water; the characteristics of chemical element transport to watercourses; and the spatiotemporal (different time intervals—season, days, hours) distribution, migration, and speciation of metals in river water. In addition, studies were carried out (in Saransk and Temirtau) on the chemical composition and geochemical features of urban sewage sludge (SS), industrial slurries, and industrial dust (dust from processes, ventilation, and industrial premises) from various enterprises; area-based soil sampling (250 × 250 m grid) was done in Saransk and Temirtau; and the composition of some types of solid industrial waste was studied (Saransk, Temirtau). Methodological aspects and the main results of these studies are described in (Saet et al., 1990; Saet and Yanin, 1984; Yanin, 1992, 2003b). In the Moscow region, a total of 1900 river sediment samples, 295 river water samples, 175 river SPM samples, 175 river separation SPM samples, 15 river sludge water samples, 15 river bottom water samples, 60 lake sediment samples, 160 lake water samples, 160 lake SPM samples, and 20 lake silt water samples were taken; in the Kazakhstan region, 1600 bottom sediment samples, 1800 soil samples, 80 industrial waste samples (sewage sludge, industrial slurries, slag, etc.), 20 samples of dust from industrial premises, 300 surface water samples, 150 river SPM samples, 24 separation SPM samples, and 15 sludge water samples; in the Mordovia region, 650 bottom sediment samples, 1600 soil samples, 26 separation suspension samples, 20 SS samples, 15 industrial slurries samples, 425 samples of soil samples from industrial zones, 70 industrial dust samples, 210 surface water samples, and 210 river SPM.

Statistical processing of the factual material involved calculating the standard distribution parameters of chemical elements in a particular component: the average content of elements (arithmetic average), the variation coefficient (standard deviation and variation range), correlation coefficients, etc., as well as various geochemical and ecogeochemical indicators.

Technogenic geochemical anomalies recorded by river sediments usually have a multielement composition, i.e., an increased (anomalous) accumulation of a certain group of chemical elements in sediments. This group of chemical elements characterizing the composition of the geochemical anomaly (in fact, the composition of technogenic pollution) and, accordingly, the geochemical (migration) flow associated with the source or several sources of technogenic impact on the studied watercourse, is called the technogenic geochemical association (Sayet et al., 1980 ; Sorokina et al. 1980). Spatially, the geochemical association is able to characterize the object (watercourse) of study as a whole, a part thereof, or a specific sampling point. Detection of technogenic geochemical anomalies and analysis of chemical element associations (geochemical associations) were based on the study of geochemical samples, i.e., the aggregate concentrations of elements in bottom sediments (and other components of the aquatic medium), confined to a specific part of the riverbed directly impacted by a source (groups of sources) of pollution.

The following indicators were used to characterize technogenic geochemical associations in river bottom sediments (and other sedimentary formations) (Yanin, 1999, 2002b).

(1) The concentration coefficient of a chemical element, K_C, which characterizes the concentration level (intensity of an anomaly) of an element in sediments (in the pollution zone) with respect to its background (natural) content (or global distribution parameter—average content in sedimentary rocks, the lithosphere, etc.). The association includes elements with K_C values no less than 1.5. This level, to a certain extent, smoothes the natural variation in the chemical element distribution and possible errors involved with

Table 1. Hazard classes of chemical elements in water objects involved with household, cultural, and community water use (Predel'no-dopustimye..., 1998)

Hazard class		
1 (extremely hazardous)	2 (highly hazardous)	3 (hazardous)
Be, Hg, Tl	Ag, Al, As, B, Ba, Bi, Br, Cd, Co, F, Li, Mo, Nb, Sb, Se, Sr, Te, Pb, W	Cr, Cu, Mn, Ni, Ti, V, Zn

Elements of hazard classes 1 and 2, as well as Cr, Ni and V, are standardized according to the sanitary–toxicological hazard indicator; Mn and Cu, by the organoleptic indicator; Ti and Zn, by the general sanitary indicator; the limiting hazard indicator is taken into account when several substances are simultaneously contained in water and when calculating total indicators.

sampling and analytical studies. In addition, in the main types of rocks that control the geochemical features of natural (background) landscapes, most chemical element concentrations are characterized by a relatively uniform spatial distribution (variation coefficients are usually within 30–60%); only at times is a nonuniform distribution (60–100%) (Printsipy..., 1979). Thus, element concentrations in bottom sediments 1.5 times higher than the background contents can be referred to with a high degree of confidence as abnormal.

The concentration coefficient is calculated by the formula

$$K_C = C_i/C_B,$$

where C_i is the average concentration of the ith chemical element established for a given geochemical sample and C_B is its background content.

(2) The geochemical association formula characterizes the qualitative (elemental) composition and structure of the geochemical anomaly; it is ordered by the K_C values (ranked range) for the entire set of chemical elements. As a rule, an association characteristic of a certain type (source) of impact is identified by a peculiar quantitative combination (the ratio of K_C values) of elements. The geochemical association formula is depicted, e.g., as follows:

$$\mathrm{Hg}_{150}–\mathrm{Cd}_{110}–\mathrm{Ag}_{78}–\mathrm{As}_{51}–\mathrm{Zn}_{23}–\mathrm{Pb}_{11}–(\mathrm{Cu}–\mathrm{Co}–\mathrm{Sb})_{5}–\mathrm{Mo}_{3}–(\mathrm{Mn}–\mathrm{Ti})_{1.7}–\mathrm{V}_{1.5},$$

where numerical indices near chemical element symbols represent their K_C. Usually the chemical elements included in the association are combined by K_C values into groups, the interval bounds of which approximately correspond to the scale of common logarithms with a step of 0.5, 1.5–3, 3–10, 10–30, 30–100, etc., which is evident when comparing various objects and tabulating materials.

(3) The indicator N_e characterizes the quantitative composition of the technogenic geochemical association and reflects the number (amount) of its chemical elements.

(4) The total pollution index Z_C (Saet, 1982) is the sum of the concentration coefficients K_C of elements (minus the background) included in the geochemical association; it reflects the cumulative excess of the background level by the group of associated elements and characterizes the level of technogenic pollution of a watercourse. It is calculated by the formula

$$Z_C = \left(\sum_{i=1}^{n} K_C\right) - (n-1),$$

where K_C is the concentration coefficient of the ith chemical element; n is equal to the number of chemical elements included in the geochemical association (i.e., N_e).

(5) The sanitary–toxicological hazard indicator Z_{ST} is the sum of the concentration coefficients K_C (minus the background) of elements of the first and second hazard classes included in the association, for which the maximum allowable concentrations (MAC) in waterbodies have been established (Table 1). It characterizes the degree of potential sanitary–toxicological hazard of a given level of industrial pollution. In this case, we are talking about the sanitary–toxicological hazard of bottom sediments as a substances. This indicator is calculated using the same formula as the total pollution indicator Z_C (with appropriate correction for the considered chemical elements).

(6) The characteristics of technogenic pollution level and its degree of potential sanitary–toxicological hazard based on an indicative scale (Table 2). This scale is of an expert-determined nature: it was devised based on empirical material obtained by a joint study of technogenic geochemical anomalies in bottom sediments and in a solution of river water. Nevertheless, experience has shown the effectiveness of its application. The degree of sanitary–toxicological hazard of technogenic pollution governs the significance of sediments as a source of pollution of the aqueous phase and the likelihood of their toxic (as a substance) impact on living organisms.

Table 2. Approximate scale for assessing river pollution based on intensity of chemical element accumulation in bottom sediments (Yanin, 2002b)

Z_C	Z_{ST}	Level of technogenic pollution	Degree of sanitary–toxicological hazard	Toxic element content in river water solution
<10	<10	Weak	Allowable	Majority within background
10–30	10–30	Average	Moderate	Many are elevated with respect to background; some occasionally reach MAC
30–100	30–100	High	Hazardous	Many noticeably above background; some exceed MAC
100–300	100–300	Very high	Very hazardous	Many are many times above background; some stably exceed MAC
>300	>300	Extremely high	Extremely hazardous	Most are many times above the background; many stably exceed MAC

Calculation of Z_C should be based on a study of the distribution of at least 40 chemical elements in bottom sediments.

Refinement of the methodologies for collecting various samples, their processing, chemical-analytical studies, methods and techniques for processing factual data, and (if necessary) additional description of the areas and objects of study are given below when discussing the results obtained.

FEATURES OF RIVERBED SEDIMENTS IN NATURAL CONDITIONS

Under natural conditions, the formation of channel alluvium is determined by the character and intensity of soil and rock erosion in catchment areas, and by the transport, accumulation, and redeposition of sedimentary material (river sediments) by water flows, the total volume of which is the complex of erosion–accumulation processes, involving soil erosion, gully erosion, and channel processes (Makkaveev and Chalov, 1986). Erosion processes in catchment areas are the most important factors in the transport of natural sedimentary material into rivers, the development of river channels, and the formation of alluvial sediments. The intensity of erosion depends on the type of relief and ground cover, rock composition, the amount and type of precipitation, the magnitude and regime of water flow, infiltration rates, etc. The relationship between erosion and accumulation is particularly well illustrated in perennial watercourses, the competence of which is determined by their flow velocities and depends on their water content, steepness of slope, and the intensity of alluvium-forming sedimentary material delivered to the riverbed. In alluvial sedimentation, depending on the direction of movement of the Earth's crust, the relief, climate, and water flow regime, only the dynamics of the accumulation process change, which also governs the degree of development and structural features of alluvial strata. The most differentiated and typically built up is alluvium of large and medium lowland rivers belonging to humid zones.

Among lithological types of channel sediments, fine-grained sands usually dominate. A thin layer of silty (sandy-silty) sediments often forms on point bars. Channel silts proper are of subordinate importance and are usually found in backwaters and the wide parts of rivers. About 80 terrigenous minerals are found in the channel sediments of lowland rivers, with their composition dominated by quartz (up to 85–95%); feldspar (5–10%) and detrital rocks (up to 2%) are present; among the light-fraction minerals are also orthoclase, microcline, plagioclase, and glauconite; the heavy fraction is dominated by the assemblage ilmenite–garnet–hornblende–epidote (Lazarenko, 1964). Clay minerals may be present in the alluvial fine fractions. Under particular sedimentation conditions, alluvium contains diagenetic mineral formations. The chemical composition of channel alluvium is close to that of rocks that make up the catchment area (Tables 3, 4); it is almost always distinguished by a high (up to 70–80% or more) silica content, a consequence of its mineral composition. Concentrations of most chemical elements in alluvium (both in its sandy and silty varieties) are close to their average concentrations in sedimentary rocks and the lithosphere (Table 5).

Organic matter in river sediments is genetically similar to that of soil and sedimentary rocks of catchment areas (Brownlow, 1984). It includes plant debris tissues, roots, bacterial and fungal cells, their microorganism-decomposition products, and dispersed colloidal matter. As a rule, its content in modern alluvium is low. LOI values are usually 1–5%. In alluvium of the rivers of the European plain, C_{org} (organic carbon content) is up 0.04–0.52% in sands, 0.34–1.55% in silts, and 0.30–2.88% in pelites (Lazarenko, 1964). C_{org} in Pakhra riverbed sediments varied within 0.5–1.2%.

Sedimentary rock theory hypothesizes that the conditions existing in each sedimentation setting determine the properties of the sediments formed there. The concept of "sedimentation setting" includes the place where sedimentary material accu-

Table 3. Chemical composition of sandstones and background channel alluvium of different rivers, %

Component	Sandstones*	Nura	Pakhra	Insar	Alatyr	Sura
SiO_2	73.58	79.90	78.50	83.63	80.47	79.27
TiO_2	0.34	0.24	0.47	0.33	0.43	0.49
Al_2O_3	6.55	6.66	4.58	5.22	5.60	5.84
Fe_2O_3	2.10	1.28	2.68**	2.03	2.33	2.89
FeO	0.94	1.41	–	0.57	0.80	1.00
MnO	0.044	0.06	0.07	0.078	0.056	0.06
CaO	5.23	1.35	3.17	0.78	0.68	0.78
MgO	1.94	0.62	1.27	0.37	0.59	0.79
Na_2O	0.30	2.94	0.71	0.56	0.68	1.08
K_2O	2.36	3.36	1.61	1.05	1.48	1.68
P_2O_5	–	0.07	0.27	0.19	0.18	0.18
H_2O^-	–	0.26	0.82	1.37	1.45	1.55
LOI***	2.22	1.73	2.07	3.66	4.56	3.56
S_{free}	–	<0.1	0.02	<0.1	<0.1	<0.1
S_{total}	–	<0.1	0.04	<0.1	<0.1	<0.1

* Russian Platform Quaternary deposits (Ronov et al., 1963); ** total Fe_2O_3 + FeO; ***loss on ignition.

Table 4. Petrochemical modules of channel sediments and sandy rocks

Modules*	Sandy rocks	Insar	Alatyr	Sura
Hydrolysate, $Al_2O_3 + TiO_2 + Fe_2O_3 + FeO/SiO_2$	0.08	0.05	0.06	0.07
Aluminosilicate, Al_2O_3/SiO_2	0.05	0.04	0.04	0.04
Potassium, K_2O/Al_2O_3	0.36	0.23	0.29	0.31
Maturity, SiO_2/Al_2O_3	19	27	24	23
Degrees of differentiation, $SiO_2/Na_2O + K_2O$	43	67	50	37
Maturity indicator, $Al_2O_3/SiO_2 + MgO + K_2O + Na_2O$	0.05	0.04	0.04	0.04
Oxidation, Fe_2O_3/FeO	1.02	1.6	1.3	1.3
SiO_2/R_2O_3	16	22	19	18
CaO/MgO	1.95	1.6	0.9	1.4
Ferritization, $Fe_2O_3 + FeO/SiO_2$	0.02	0.01	0.02	0.02

* Based on data of Table 3; hereinafter, the moduli were calculated after (Efremova and Stafeev, 1985).

mulates, the physical, chemical and biological conditions that characterize the sedimentation environment, and the process resulting in accumulation of material (Usloviya ..., 1974). Of particular importance are the sources and transport routes of sedimentary material in the sedimentation zone.

In general, under natural conditions for channel alluvium, a rather limited set of lithologic- petrographic types of sediments is observed, represented mainly by sandy varieties, which are characterized by predominant monomineralic quartz sands with a high degree of differentiation of sedimentary material and high silicon contents. The concentrations of most chemical elements in alluvium are within their global distribution parameters in sedimentary rocks and the lithosphere. Changes in the sources of sediment supply to rivers and the environmental conditions of alluvial sedimentation are accompanied by transformation of their morphological appearance, composition, and geochemical properties, which is especially characteristic of industrial–urbanized areas.

GENERAL RIVER SEDIMENT FORMATION CONDITIONS IN TECHNOGENIC LANDSCAPES

The formation of water runoff in technogenic landscapes is determined by their hydrological features, reflecting the specifics of the water balance of eco-

Table 5. Background concentrations of chemical elements in riverbed alluvium of different rivers

Element	Pakhra River		Moscow River, mg/kg	Nura River				*A*, mg/kg	*B*, mg/kg
	mg/kg	*V*, %		sand deposits		silt deposits			
				mg/kg	*V*, %	mg/kg	*V*, %		
Li	23	50	28	26	36	34	23	56	32
Be	1	47	–	2	56	2	67	–	3.8
B	18	41	20	11	19	15	40	–	12
Sc	2.6	38	1.8	1.1	42	2.7	49	10	10
Ti	2960	29	1900	1110	21	1750	25	3800	4500
V	75	73	35	168	30	175	21	105	90
Cr	51	40	30	51	82	65	47	72	83
Mn	635	48	470	221	37	275	39	770	1000
Co	4.9	49	3.5	9.1	36	16	18	14	18
Ni	18	54	16	25	65	27	46	52	58
Cu	30	39	23	73	59	80	25	33	47
Zn	123	62	75	38	34	70	33	95	83
Ga	9	42	6	13.4	23	12	26	18	19
Sr	31	85	35	42	26	55	33	320	340
Y	18	45	11	3.5	26	4.6	24	–	29
Zr	290	30	240	30	75	31	78	–	170
Nb	10	35	7	3.5	27	3.3	31	13	20
Mo	0.83	73	0.65	1.6	49	2.2	79	2	1.1
Ag	0.02	88	0.03	0.05	27	0.078	31	0.057	0.07
Sn	4.7	63	3	3.7	26	2.9	19	4.6	2.5
Sb	3	90	–	1.3	77	1.5	67	1.2	0.5
Ba	93	59	110	270	36	160	31	460	650
Yb	2.3	34	1.5	1	75	1	85	–	0.33
W	1.8	90	–	1.5	85	2.1	75	1.7	1.3
Hg	0.01	85	–	0.044	88	0.14	75	–	–
Pb	29	44	22	32	25	35	23	19	16
Number of samples	85		50	59		25		–	–

V, %, variation coefficient, %; *A*, average content in sedimentary rocks (Bowen, 1979); *B*, the average content in lithosphere (Vinogradov, 1962).

nomically developed territories, resulting from climatic factors, the peculiarity of the formation conditions, and the regime of surface, ground-, and subsurface water runoff, water consumption, and wastewater discharge. An important feature of such landscapes is large volumes of water in relatively small areas, which, after its use for economic needs, acquires other properties, contains huge masses of sedimentary material and, as a rule, is discharged into the hydrological network.

In industrial–urbanized areas, there are two groups of pollution sources that govern the main methods of sediment supply to rivers (Fig. 4). The first group is point sources that discharge wastewater into watercourses via sewer systems (sewage). The second group combines nonpoint (area) sources of pollution, among which runoff from melt, rain, and irrigation waters from developed territories, as well as soil and ground water (surface runoff), are the most important.

The qualitative and quantitative characteristics of the city sewage runoff depend on the city's population, the characteristics of its industrial infrastructure, and systems for the collection, treatment, and disposal of wastewater. The qualitative and quantitative parameters of surface runoff are determined by the city's hydrological features, its size, and facilities; they depend on the intensity of pollutants entering the underlying surface, its characteristics, and systems for the waste collection and cleaning of urban areas. In some cities, snowmelt, polluted groundwater discharge, and water transport are of particular importance. Direct supply of pollutants

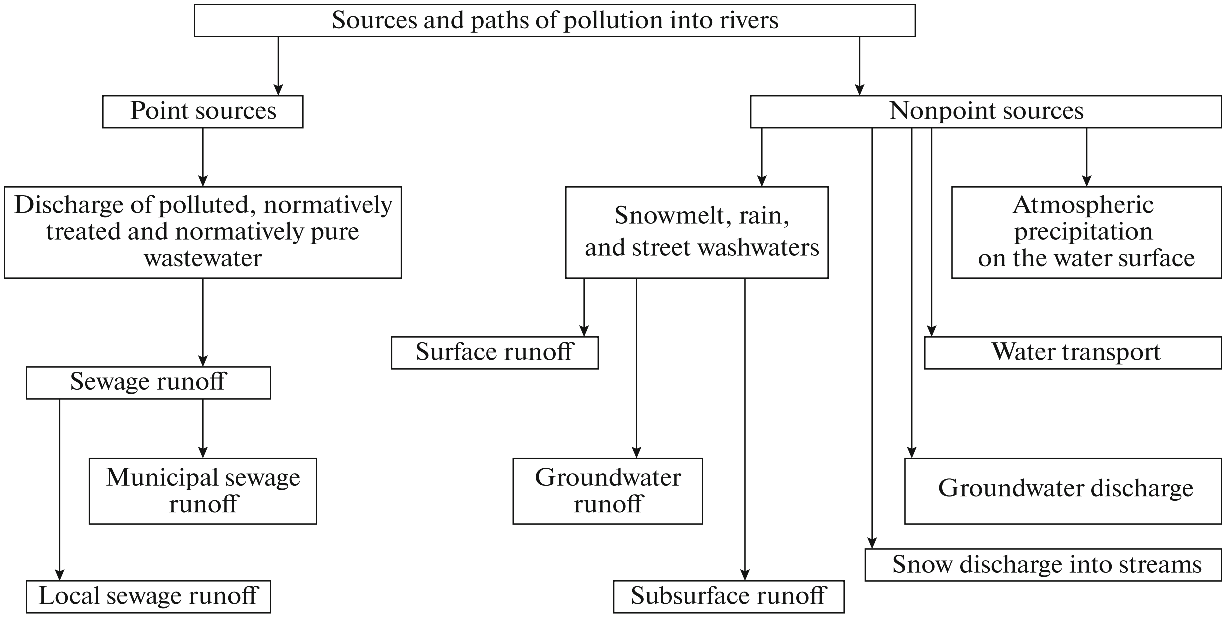

Fig. 4. Main sources and paths of pollutants entering rivers of technogenic landscapes.

to rivers with aeolian sediments is insignificant, but it plays an important role in forming the qualitative composition of surface runoff.

Urban sewage is characterized by high contents of suspended and dissolved forms of many chemical elements and compounds (Yanin, 2002b), often many times higher than their background levels in river waters (Table 6).

Sewage sludge running directly into watercourses from industrial treatment plants (local sewage) is also distinguished by high contents of a wide group of chemical elements (Yanin, 2002a). This is particularly well illustrated by the composition of industrial slurries formed at the wastewater treatment plants of various enterprises (Yanin, 2017c) (Table 7). Slurries (as well as sewage sludge generated at city treatment plants) are characterized by a peculiar petrochemical composition (Table 8). It is indicative that the average chemical composition of slurries is close to that of sewage sludge. The data also indicate that silts formed in a riverbed below a city largely inherit the composition of technogenic silts and SS.

Sewage entering watercourses is characterized not only by much higher specific chemical element concentrations, but also by concentrations differing from background river water, and by the ratio of their two main forms of migration—dissolved and suspended (Table 9). Clearly, a significant increase in the share of suspended forms of Cu, Zn, Sn, Cd, Hg, and, to a lesser extent, Cr and V is observed near sources of pollution (transects 2 and 3). Ni and Mo are exceptions, which are characterized by a predominance of dissolved compounds, which is obviously controlled by the wastewater treatment conditions. A change in the ratio of suspended and dissolved forms of elements (with an increase in the suspended form for many) in wastewater is observed in the zones of influence of other cities (Table 10). A peculiarity of sewage runoff is also observed in the change in the ratio of forms of migration of water in solution and metal speciation in SPM. Thus, for dissolved forms in wastewater, (compared with the background) a noticeable decrease in the relative share of organic Ni and Cu compounds is observed, along with an increase in the indicated forms of cadmium (Table 11). The balance of dissolved forms of Zn remains virtually unchanged. In wastewater SPM, there is a noticeable increase in the share of Ni hydroxides and a decrease in sorption—carbonate compounds, as well as a sharp increase in the share of sorption—carbonate and organomineral forms of copper (with a decrease in the share of other forms) (Table 12). The wastewater discharged into watercourses is also distinguished by temporal variability of the composition vs. high concentrations of macro- and microcomponents. Suspended and dissolved forms of metals are characterized by an irregular ratio of their concentrations with time. This indicates a temporally heterogeneous pollutant supply to watercourses.

Surface runoff from urban areas is characterized by high levels of suspended solids, heavy metals, nutrients, petroleum products, and certain organic substances (Yanin, 2002a, 2007b; Bradford, 1977). Industrial dust plays a particularly significant role in the composition of surface runoff; it enters the environment with factory emissions (Yanin, 2003a) (Table 13). These emissions result in technogenic geochemical anomalies in urban soils (Yanin, 2009) (Table 14). The chem-

Table 6. Chemical composition (dissolved forms) of water of Cherny Creek, which receives wastewater from Podolsk wastewater treatment plant

Component	Average	Limits	Background in river waters of Moscow oblast
SPM	53.1	8.7–238.6	16
NH_4^+	19.8	6.5–45.0	1.29
NO_2^-	2.0	0.6–4.0	0.081
NO_3^-	1.34	0.4–2.4	1.53
PO_4^{-3}	0.63	0.37–1.0	Trace amounts
SO_4^{-2}	2.66	40.0–75.0	27
Cl^-	91.31	81.0–133.0	8.1
K^+	15.5	8.0–20.0	3.4
F	731	300–800	216
Ti	27	10–151	6.9
V	1.4	1–8	1.14
Cr	10	1–36	3
Mn	52	16–173	25
Ni	59	1–102	1
Cu	86.6	5.2–163	8.2
Zn	51.2	15.6–86.8	28.35
Se	0.297	0.20–0.40	0.126
Zr	4	1–8	Trace amounts
Ag	–	Trace amounts–1.25	0.26
Cd	36.11	0.22–72	0.24
Sn	2.5	0.1–52	0.5
Ba	96	18–190	24.1
Hg	0.73	0.28–1.6	0.066
Pb	16	1–24	3

SPM, main ions, and nutrients—mg/L; all others, μg/L. Data for 32-day continuous observation period are presented.

ical elements contained in emissions and soils actively enter migration flows and surface runoff.

A higher coefficient of runoff from urban areas, along with high water turbidity, results from the fact that the modulus of solid runoff in technogenic landscapes far exceeds analogous indicators for natural territories (Table 15). According to (Last, 1981), sediment runoff from water collectors under construction ranges from 300 to 2200 t km^{-2} yr^{-1}, which exceeds that from natural lands by 2–100 times.

In different cities, the ratio of the above two groups of sources of pollutants in waterbodies may differ, but, all else being equal, the presence of significant impermeable areas and a drainage network significantly increases the role of surface runoff as a source of sediment supply to rivers. In medium-sized and, especially, small towns, the main impact on watercourses is often associated with sewage sludge.

Deep underground (artesian) waters impact the composition of surface waters in cities where they are heavily used for drinking and industrial water supply. In some cases, they can additionally transport to urban wastewater a number of major ions (sodium, sulfates, chlorides) and certain chemical elements (Yanin, 2009a).

Technogenic impact causes a unique alluvial sedimentation setting (Yanin, 2003b, 2006a). Surface waters here are distinguished by increased contents of main ions (Table 16), as well as disruption of their quantitative relationship characteristic of background conditions. Naturally, salinity of surface waters also increases substantially.

A transition of waters with average salinity typical for a given natural region into waters with elevated and even high salinity (i.e., brackish waters) is observed everywhere. Surface bicarbonate waters occur (often with a hydrocarbonate concentration >250 mg/L) with a salinity exceeding 1000 mg/L, which are very

Table 7. Association of chemical elements in industrial slurries and urban sewage sludge (SS), city of Saransk (Mordovia)

Factory*	Concentration coefficients of chemical elements (K_C) with respect to content in background soils							Z_C
	>1000	1000–300	300–100	100–30	30–10	10–3	3–1.5	
SCP	Sn_{8750}–Bi_{2750}–Au_{2500}–Ag_{2000}	–	F_{185}	Ni_{68}–Cu_{60}–Mo_{54}–Cr_{40}–Zn_{37}–Pb_{35}–Cd_{34}	W–P	B	Co–Sr	16 535
SLBF	Hg_{5000}–Mo_{1583}	Bi_{950}–Sb_{600}–Cd_{571}–Ni_{300}–Cu_{277}–W_{260}	Ag_{140}	Sn_{45}–Pb_{35}	Tl–Cr–PFB–Sr	Zn	Ba–Mn	9857
RT	Bi_{3750}–Cu_{1667}	–	Zn_{144}	Sr_{44}–P_{10}	Cd–Sn–Cr–Pb–Ge–Ni–Mo–Ag	F–Fe–Sb	W–B–Co	5768
LP	Au_{5000}	–	W_{253}–Sn_{250}–F_{206}	–	Ni	Mo–Cu–Sb	Pb–Ag	5741
EE	Mo_{1333}–Cd_{1143}	Bi_{800}–Sn_{425}–Ag_{400}	Cu_{267}–Zn_{144}	Ni_{74}–W_{67}–F_{40}	P–Cr–	B–Pb–Sb	Sr	4708
Mech	–	Sn_{750}–Cr_{343}–Pb_{131}	Cd_{229}–Ag_{168}–Cu_{113}	Mo_{83}–Bi_{75}–Zn_{56}–P_{44}–Sb_{30}	W–F–Ni	–	–	2260
SLS-EVG	–	Zn_{942}–$F_{45}0$–Cu_{433}	$Ni_{160}Mo_{108}$	Pb_{33}	Cr–WP	Ag–Cd–Be–Sb	Sr–Sn–B	2183
TF	–	Sn_{500}–Cr_{343}	Mo_{108}	Cu_{80}	F–Ni	Pb–Ag–W	B	1055
CB	–	–	–	Sn_{60}	Sr–Ag	Cd–Pb–Cu–B–Hg–Sb	F–W–Mo–Ni	112
MP	–	–	–	Cu_{33}	Sn–P–Zn–Cd	Be	Mo–F–Ag–W–Pb	80
CT	–	–	–	–	Sn	Pb–Mo–W–Hg–Ag–Cu	Zn–B–Cr	64
CS	–	–	–	–	Pb	Cu–W–Zn–Hg–Sn–Ag–P–Be–F–Sb	Mo	51
AF	–	–	–	–	Cd–Pb–Sn	Cu–Zn–Ag–Be–Sb–Mo–WF–	–	50
SS	Bi	Cd	Sn–Ag	Zn–Mo–Hg–W–Cu–Sb	P–Cr–Pb–Ni	As–F–Yb	B–Sr–Be	2555

* Abbreviations of enterprises: AF, auto factory; TF, tool factory; Mech, mechanical plant; MP, meat processing plant; SCP, semiconductor product plant; RT, rubber technology; CT, construction transport; SIS-EVG, Special light sources and electrovacuum glass; SLBF, Saransk light bulb factory; LF, Diesel locomotive repair plant; CS, cold-storage plant; CB, city central boiler house; EE, electric eliminator.

Table 8. Chemical composition of industrial slurries, sewage sludge (SS)*, technogenic silts (TS)** and background alluvium (BA)***, %

Component	Industrial slurries of Saransk enterprises****									SS	TS	BA
	SCP	SLS-EVG	SLBF	LP	RT	AF	CT	MP	average			
SiO_2	2.43	6.33	2.72	1.50	19.99	59.14	65.83	6.50	20.6	23.87	58.42	81.63
TiO_2	0.04	0.03	0.02	0.03	0.15	0.28	0.36	0.04	0.12	0.25	0.64	0.33
Al_2O_3	1.17	1.62	0.50	2.20	2.22	4.60	6.45	0.70	2.44	4.70	10.98	5.22
Fe_2O_3	3.26	3.75	1.39	0.34	28.31	3.60	3.84	1.02	5.69	1.04	3.73	4.03
FeO	0.21	0.14	0.10	<0.10	–	–	–	–	–	3.00	2.66	0.57
MnO	0.04	0.03	0.21	0.01	0.15	0.05	0.05	0.02	0.07	0.05	0.08	0.08
CaO	28.26	32.03	41.96	28.10	10.68	8.93	5.85	4.00	19.98	8.00	2.20	0.78
MgO	16.88	10.54	6.72	25.70	6.75	2.92	1.51	0.40	8.93	1.40	1.36	0.37
Na_2O	0.50	0.25	0.35	0.20	0.60	0.50	0.60	0.50	0.44	0.58	0.92	0.56
K_2O	0.10	0.10	0.15	0.10	0.10	0.90	1.20	0.20	0.37	0.84	1.89	1.05
P_2O_5	2.86	1.50	4.24	0.04	8.80	0.36	0.19	3.50	2.69	3.00	0.62	0.19
H_2O^-	5.66	7.46	3.30	4.70	6.60	1.40	1.42	6.20	4.59	4.81	2.58	1.37
LOI	33.68	31.67	36.00	34.14	12.84	16.82	12.20	75.50	31.61	46.08	13.23	3.66
S = 0	0.99	–	0.68	0.19	0.34	<0.10	–	0.43	0.33	0.89	0.16	<0.10
Total	98.23	95.45	98.56	99.74	97.53	99.50	99.50	99.01	–	98.51	99.47	99.84
S_{tot}	198	–	1.37	0.39	0.68	<0.10	–	0.86	0.66	1.79	0.32	<0.10
CO_2	17.60	17.16	27.28	17.16	3.52	8.14	4.18	0.22	11.90	2.75	1.32	0.66
F	3.70	9.0	0.37	4.12	0.08	0.04	0.02	0.04	2.17	0.33	0.05	0.02

* Saransk city treatment facilities; ** Insar River below sewage treatment plant; *** Upper reaches of Insar River; **** for abbreviations, see legend in Table 7.

Table 9. Metals in surface waters in zone of influence of Saransk

Metal	Transect 1				Transect 2				Transect 3			
	D	S	C	%	P	S	C	%	D	B	C	%
V	1.14	3	4.14	73	1.5	8.7	10.2	85	1.4	7	8.4	83
Cr	3	3	6	50	35.2	194	229.2	85	37	90	127	71
Ni	2.6	1.9	4.5	42	64	35	99	35	30	12.5	42.5	29
Cu	7.6	1.9	9.5	20	6	125	131	95	5	65	70	93
Zn	15	7.2	22.2	32	36	58	94	62	22	125	147	85
Mo	0.5	1	1.5	67	149	240	389	62	115	40	155	25
Cd	0.24	0.36	0.6	60	0.5	5	5.5	91	0.5	2	2.5	80
Sn	0.5	0.9	1.4	64	4.8	240	244.8	98	2.9	220	222.9	99
Hg	0.07	0.02	0.09	22	0.1	0.41	0.51	80	0.05	0.25	0.3	83
Pb	2.2	3.5	5.7	61	6	11	17	65	5	8	13	62

Forms of migration, µg/L: D, dissolved; S, suspended; T, total P + B; %, share of suspended forms of specified amount, %; average data for 8-day observation period are given; transects: 1, background, upper reaches of Insar River; 2, mouth of Nikitinsky Creek receiving runoff from local treatment facilities (Saransk central industrial zone); 3, mouth of discharge channel through which wastewater from city wastewater treatment plants flows into Insar River.

Table 10. Metals in water of Cherny Creek, which receives sewage runoff from Podolsk and flows into Pakhra River*

Metal	Black Creek		Pakhra River, background	
	total, µg/L	proportion of suspended forms, %	total, µg/L	proportion of suspended forms, %
Cr	39.54	75	8.39	64
Ni	85.15	31	5	80
Cu	160.23	46	12.8	36
Zn	121.04	58	42.95	34
Cd	39.33	8	0.64	63
Hg	1.282	43	0.0689	4
Pb	79.5	80	8.8	66

* Data for 32-day continuous observation period are given.

rarely encountered in nature, as well as water with a salinity >10 000 mg/L and an HCO_3^- content less than 10 mg/L, with significantly predominant sodium and potassium concentrations. Sodium, sulfates, and chlorides usually dominate in the composition of waters. An even more significant increase in concentrations is observed for nutrient compounds. The change in the mode of main ions is accompanied by a transformation of the zonal chemical composition of river waters, which forms a pronounced spatial mosaic of the geochemical appearance of watercourses (hydrochemical variegation), when river waters of different chemical class, form, and type exist simultaneously within a catchment area that is relatively homo-

Table 11. Dissolved forms of metals in sewage runoff of Podolsk

Metal	Sewage runoff				Background river water	
	total	org	inorg	%	total	%
Ni	56.09	10.21	45.88	18	8	50
Cu	40.08	7.3	33.60	18	7.4	37
Zn	50.73	11.40	39.27	23	32.9	20
Cd	9.25	4.40	4.85	48	0.61	5

Forms of migration, μg/L: total, sum of dissolved forms; org, organic; inorg, inorganic; %, proportion of organic form of total content, %.

Table 12. Metal speciation in sewage SPM

Metal	Place*	Gross, mg/kg	Share of form of gross, %			
			carbonate sorption	organomineral	hydroxide	crystalline
Ni	S	425	42.09	17.65	19.11	21.15
	B	40	64.26	15.30	1	19.44
Cu	S	1412	4.34	17.78	23.53	54.35
	B	50	33.33	40.51	11.86	14.30

* S, Black Creek receiving sewer runoff from Podolsk; B, background streamflow.

Table 13. Association of chemical elements in dust of electrical engineering plants, Saransk

Factory	Dust*	K_C of elements relative to content in natural soils					
		>300	300–100	100–30	30–10	10–3	3–1.5
Light bulb	1	Sb–Cd	Hg–W	Pb–Sn–Ba–As	Zn–Mo–Cu–Sr–Ge	Mn–Cr–Ag	Co–B–V–Ni
	2	–	–	Pb	Hg	Zn–Cd–Cu	–
	3	Cd	Pb–Cu	Hg	Zn	Mn	–
Special light sources	1	Cu	B–Ag	Pb–Zn–	Sb–W–Bi–Cr	Ni–Cd–Mo–Co–Hg–Mn–	Ge–V–Sn–Ti
	2	Cu	Ag–Pb	Cr–Zn	Sb–Ba–Mo–Ni	Hg–Cd–Co–W–Sn–Mn	B–V–Ge–Ti–Sr
	3	Pb	–	W	Sb–Bi	Zn–Hg–B–Cu–Ga–Co–Ag–V	Mo–Sn–Ni–Ti–Cr
Electric eliminator	1	–	–	Cd–Mo–Cu	Cr–Pb–Co–Ni	Ag–Zn	Mn
	3	–	–	Pb–Mo–Zn–Cd	–	Cu–Cr–Fe	Co
Power electronics	1	Cd		Pb–Mo	–	Cr–Cu–Zn–Ag	Co
	3	Ag	Mo	Cd–Zn–Pb	Cu	Cr–Fe	Co
Power converters	1	–	–	Cu	Cd–Ag	Zn–Ni–Co–Mo–Cr–Mn	Pb
	3	–	–	Cd–pb	–	Zn	Cu–Fe–Cr
Cable	2	Cu–Sn	Pb–Sb–Cd	Zn	Ag–Bi–W	Mo–Hg–Cr–Ni	Ba
	3	–	Cu–W–Pb–Sn–	Sb	Bi–Zn–Ag	Mo–Hg	Co–Cr–Ba

* Dust: 1, process; 2, ventilation; 3, dust from workrooms.

Table 14. Geochemical associations in soils of various enterprises in Saransk

Enterprise	K_C of elements with respect to content in natural soils					
	>300	300–100	100–30	30–10	10–3	3–1.5
Light bulb	Hg	Cd	Pb–Sb–Ag	Mo–Tl–W–Zn	Sn–Cu–Ba–Cr–Ge–Bi–Co	V–Ni–Be–As–B–P
Light sources and vacuum tube glass	–	Pb	–	Hg	Mo–W–Cu–V–Zn–Sb	Cd–Ge–Cr–Li–Ag–Bi–B–Sn–Yb–F–As
Electric eliminator	–	W	Mo	Ag–Sn–Cu–Hg	Cd–Ge–Pb–Bi–Zn–Be	Co–B–V–Cr–Li–P
Mechanical	–	–	Sn	W–Cd	Bi–Mo–Pb–Cu–Co–Zn–Be	Hg–V–Cr–Yb–B–P–Ag–Li
Medication	Cd	–	–	Cu–Hg–W–Ag–	Mo–P–Be–Bi–Zn–Pb	Cr–B–V–Ni–Co–Sn–Li
Casting	–	–	Bi	–	Pb–Hg–Zn	Cu–Be–V–Co–Mo–W–Cr–Sn–B–Li
Power electronics	–	–	–	Mo	W–Bi–Pb–Be	Cd–V–Cu–Sn–P–B–P
Diesel locomotive repair	–	–	–	Pb–Zn	Sn–W–Cr–Cd–Cu–Bi–V	Be–Co–Sb–Mo–Ag–Bi–Li

Table 15. SPM in surface runoff from urban areas (Molokov and Shifrin, 1977)

Characteristics of catchment area	SPM, g/L
Modern residential development	1.4–1.5
Landscape lacking facilities (manor building dominates)	1.8–2.5
Well-maintained areas with heavy traffic and pedestrians	1.7–2.2
Areas with large industrial enterprises	1.7–2.5
Residential areas with eroded slopes or construction sites	4–6

Table 16. Frequency of anomalous (above background) concentrations of main ions and compounds of nutrients in Pakhra River water in zone of influence of Podolsk*

Component	Number of days (as % of observation period) with values exceeding background:								
	two times			five times			ten times		
	transects			transects			transects		
	I	II	III	I	II	III	I	II	III
SO_4^-	59	96	90	26	–	–	–	–	–
Cl^-	100	100	100	100	34	21	31	–	–
K^+	100	100	96	100	100	96	100	81	71
PO_4^{3-}	100	100	100	100	100	100	100	96	96
NH_4^+	100	96	100	100	84	65	100	34	21
NO_3^-	3	37	46	–	–	–	–	–	–
NO_2^-	100	100	100	100	100	100	100	100	100
Turbidity	40	9	9	3	–	3	3	–	–

* Observation period, 32 consecutive days in summer low-water period; transects: I, mouth of Cherny Creek receiving Podolsk wastewater; II, Pakhra River 2 km below Cherny Creek; III, Pakhra River 9 km below Cherny Creek.

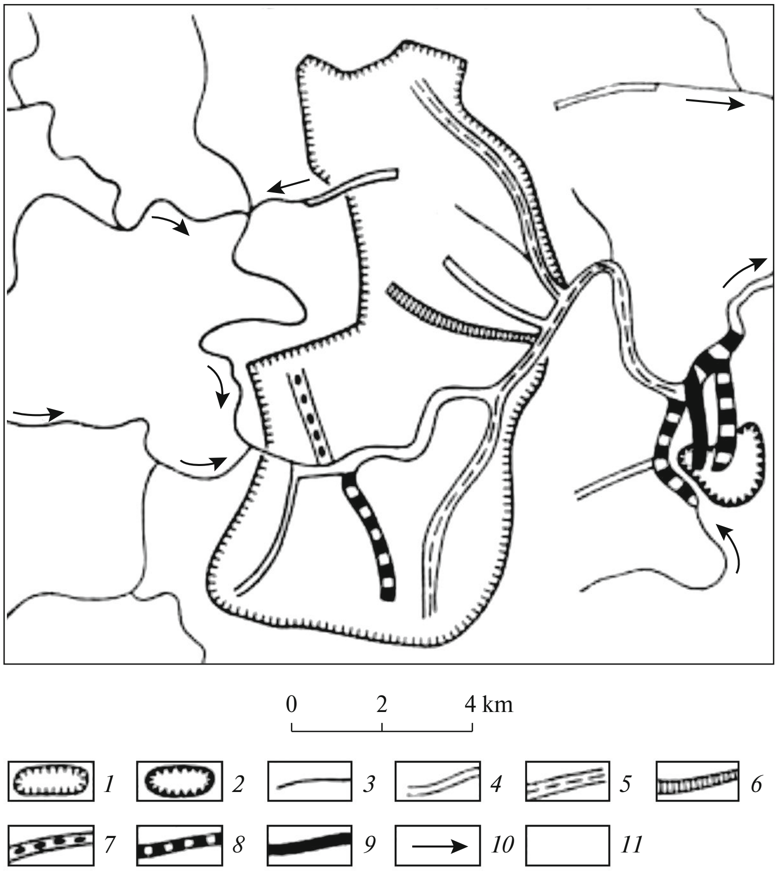

Fig. 5. Hydrochemical scheme of Podolsk and its environs: (*1*) city; (*2*) landfill; (*3–9*) type of water in watercourses: (*3*) hydrocarbonate calcium waters with salinity up to 500 mg/L; (*4*) hydrocarbonate calcium water with salinity of 500–900 mg/L; (*5*) sodium bicarbonate water with salinity of 500–900 mg/L; (*6*) calcium sulfate waters with salinity of 500–900 mg/L; (*7*) calcium nitrate brackish waters (1000–1200 mg/L); (*8*) sodium chloride brackish waters (1000–10000 mg/L); (*9*) potassium chloride brackish water (1000–1100 mg/L), (*10*) direction of flow of watercourses; (*11*) agricultural and natural territories.

geneous in its landscape and geochemical conditions (Fig. 5).

The most important feature of river waters in areas of technogenic impact is a significant increase in chemical element concentrations (Fig. 6). For a number of them, an increase (with respect to the background) in the amount (specific and relative) of suspended forms of migration is observed. This phenomenon results from both the increased turbidity of river waters and (especially) a sharp increase in specific element concentrations in river SPM.

Technogenic anomalies of suspended forms of elements are stabler with time: most of the elements are different than those in background conditions, a balance of suspended and dissolved forms (Tables 17, 18) The composition of river waters in technogenically polluted areas is also characterized by a pronounced inhomogeneous distribution of element concentrations both downstream from the source of pollution and in the observation intervals of hours, days, and seasons (Figs. 7, 8). The inhomogeneous distribution of elements in water is also manifested as an inhomogeneous ratio of their suspended and dissolved forms and speciation in river water SPM and solution. All this creates spatiotemporally physicochemically variegated river waters and variable geochemical conditions of the alluvial sedimentation setting.

The participation of significant masses of specific technogenic sedimentary material in alluvial sedimentogenesis affects sedimentation processes and leads to the intensive formation of technogenic silts in riverbeds. The geochemical conditions of the alluvial setting for technogenic sedimentation are favorable to the development sorption, coagulation, and coprecipitation processes, which are also important for the formation of technogenic silts and removal of chemical elements and their compounds from the migration flow.

CHEMICAL COMPOSITION AND FEATURES OF SEDIMENTARY MATERIAL DELIVERY WITH CITY SEWER RUNOFF

In technogenic landscapes, the solid runoff moduli increase (compared with zonal values) by one to two orders of magnitude. For example, according to official data, in the early 1990s, 20 500 t of SPM per year were delivered with Moscow wastewater to watercourses (Gosudarstvennyi doklad..., 1993). The actual supply of technogenic sedimentary material is, of course, greater (even though the above-mentioned figure is quite large). Thus, if we proceed from the fact that within the limits of Moscow in the specified period, 5 mln m^3 of runoff was delivered annually with an average turbidity of 30 mg/L, then at least 60 000 t of solid SPM came with it. The natural modulus of SPM for this area ranges from 5 to 30 t km^{-2} yr^{-1}; i.e., from an area equal in size to Moscow, 4500–27 000 t of solid material may be transported, which is appreciably less than the technogenic supply. In the Pakhra River basin, the zonal runoff modulus varies between 5–30 t km^{-2} yr^{-1} (Resursy..., 1973a), and the minimum values are typical of areas unaffected by economic activity. Calculations show that the similar indicator for the territory of Podolsk taking into account only sediment entering the Pakhra River with sewage is 40 t km^{-2} yr^{-1}. For the Insar River basin, the zonal sediment runoff modulus is estimated at 0.6 g s^{-1} km^{-2}. Within the city of Saransk, if we take into account the additional supply of solid sediments only from organized wastewater discharge, it increases to 2.4 g s^{-1} km^{-2} (Yanin, 2002c). A significant mass of sedimentary material also comes with city surface runoff, which further increases the solid sediment modulus. Sewage sludge proper is one of the most important supply sources of technogenic sedimentary material to rivers. In addition, it is fairly constant within the annual profile; i.e., its supply of

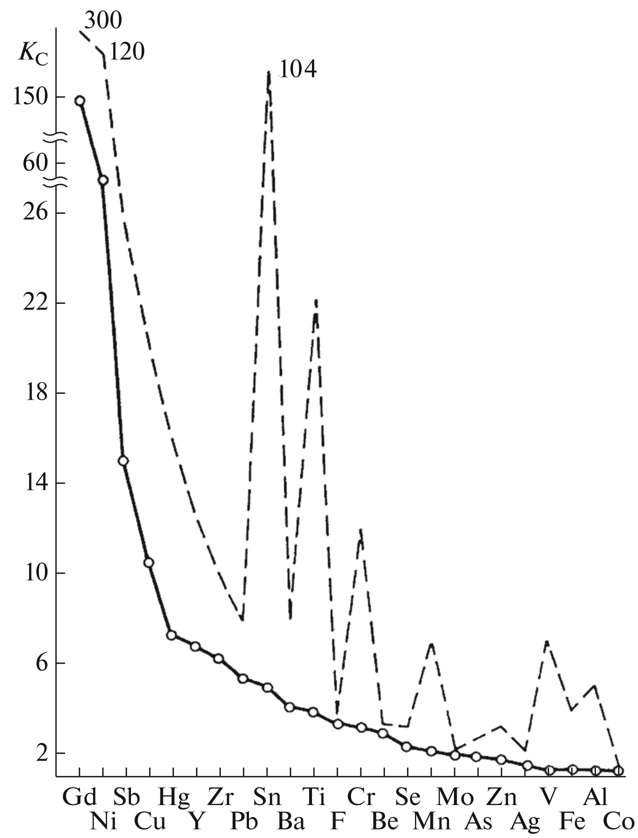

Fig. 6. Geochemical ranges in Cherny Creek, which receives runoff from Podolsk (Saet and Yanin, 1991): solid line, average K_C of dissolved forms during 30-day observation period in summer low water; dotted line, maximum K_C values for same period.

Table 17. Metals in water of mouth of Cherny Creek receiving Podolsk sewer sludge

Metal	Migration form	Average, µg/L	*V*, %	K_C	S + D, µg/L	*V*, %	K_C	Share S of S + D, %
Cr	B	29.44 ± 4.43	60	4.1	39.41 ± 7.81	57	4.7	75
	D	9.97 ± 3.41	99	8				
Ni	S	26.14 ± 7.81	86	11.6	75.55 ± 11.10	42	15.9	35
	D	49.41 ± 7.88	46	19.8				
Cu	S	73.75 ± 17.04	67	16.1	108.99 ± 17.76	47	8.9	68
	D	35.24 ± 10.15	83	4.6				
Zn	S	69.83 ± 15.05	62	5.3	118 ± 13.99	34	2.8	59
	D	48.17 ± 5.67	34	1.7				
Cd	S	3.22 ± 0.76	68	21.3	9.33 ± 5.12	158	32.9	35
	D	6.11 ± 5.06	238	45.9				
Hg	S	0.61 ± 0.21	99	321	1.34 ± 0.27	59	26.3	46
	D	0.73 ± 0.13	52	15				
Pb	S	40.00 ± 10.70	77	8.9	45.78 ± 10.73	68	6.9	87
	D	5.78 ± 2.02	101	2.7				

Tables 17 and 18 show data for 32-day continuous observation period during summer low water. Forms of migration (separation by ultrafiltration through membrane filters with pore diameter of ~0.45 µm): S, suspended; D, dissolved; S + D, total content; *V*, % is variation coefficient; K_C, concentration coefficient with respect to background.

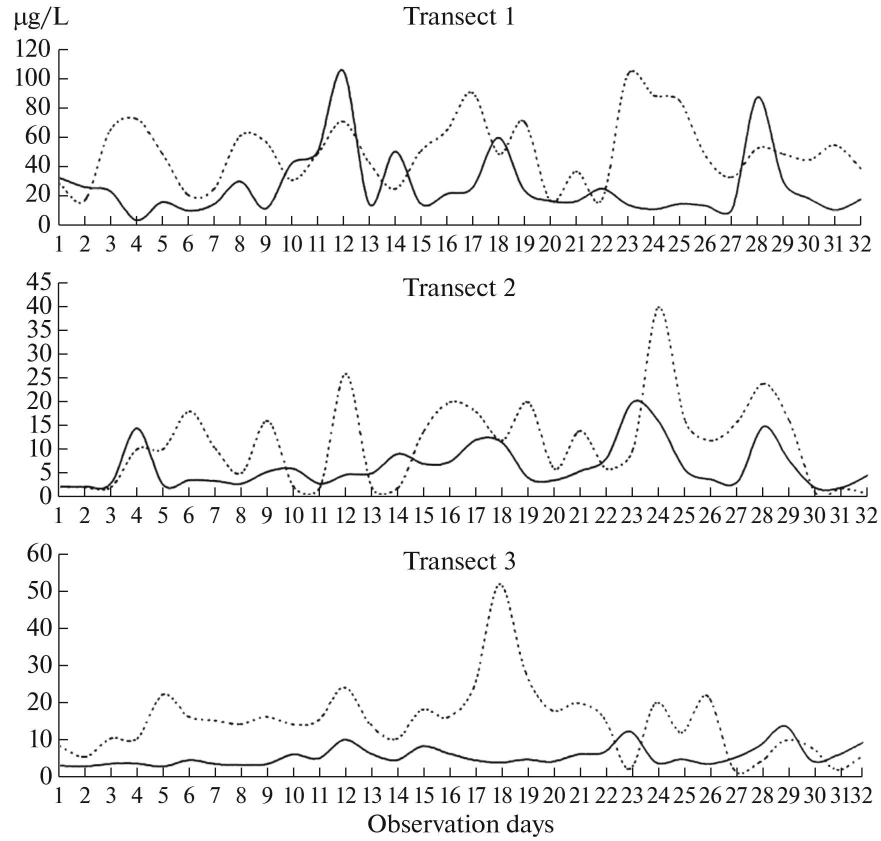

Fig. 7. Distribution of dissolved (points) and suspended (solid line) forms of nickel in surface waters in zone of influence of Podolsk. Observation transects: (1) mouth of Cherny Creek; (2) Pakhra River 2 km below mouth of Cherny Creek; (3) Pakhra River 9 km below mouth of Cherny Creek.

sedimentary material is usually independent of season and relatively stable throughout the year, whereas surface runoff is characterized by a inhomogeneous (seasonal) distribution.

In wastewater treatment, two types of technogenic sedimentary formations occur at city treatment plants: sewage sludge (most of the incoming sediment material passes into it) and technogenic sediment, which is discharged into wastewater and helps to form technogenic silts. Sewage sludge generated at a treatment plant can be considered a geochemical analog of technogenic silts.

Table 18. Metals in water of Pakhra River 2 km below mouth of Cherny Creek

Metal	Migration form	Average, μg/L	*V*, %	K_C	S + D, μg/L	*V*, %	K_C	Share of S of S + D, %
Cr	S D	10.33 ± 2.11 5.84 ± 1.97	59 97	1.5 4.7	16.17 ± 3.30	59	1.9	62
Ni	S D	6.47 ± 1.61 11.16 ± 3.14	72 81	2.9 4.5	17.63 ± 4.14	68	3.7	37
Cu	S D	15.92 ± 4.65 13.96 ± 3.73	84 77	3.5 1.8	29.88 ± 7.53	73	2.5	53
Zn	S D	26.17 ± 4.34 34.93 ± 4.98	48 41	2 1.2	61.01 ± 7.62	36	1.5	44
Cd	S D	0.75 ± 0.23 0.72 ± 0.37	90 147	5 5.4	1.47 ± 0.43	85	5.2	51
Hg	S D	0.102 ± 0.048 0.655 ± 0.174	135 77	53.7 13.3	0.757 ± 0.187	71	14.8	14
Pb	S D	13.5 ± 4.58 6.33 ± 3.17	98 144	3 2.9	19.83 ± 5.47	80	3	68

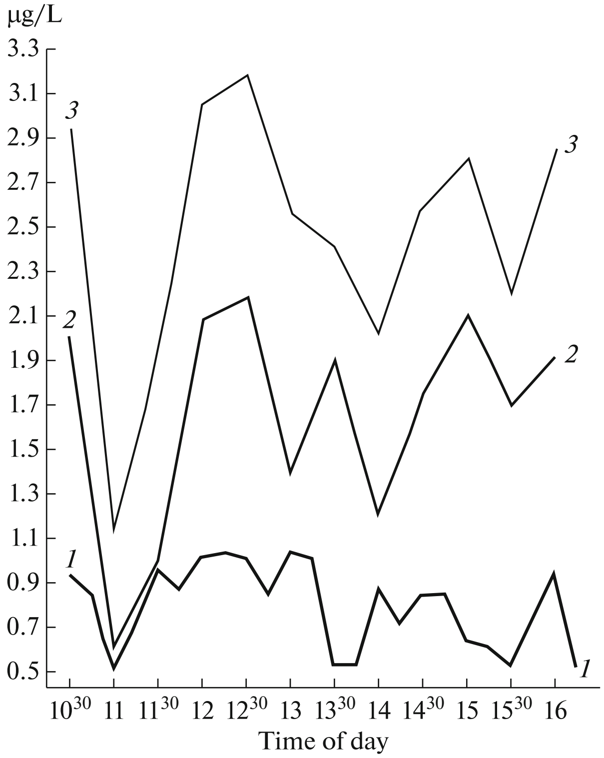

Fig. 8. Distribution of dissolved (*1*) and suspended (*2*) forms and total content (*3*) of mercury at mouth of main wastewater canal, which discharges wastewater from Temirtau into Nura River.

The behavior of SPM in river water in the zones of influence of cities is largely determined by the presence of a spatial structure in the water flow resulting from a typical interlink in practice: the source of pollution (city treatment plants discharging wastewater), a sewage runoff reservoir (usually a small watercourse), and a small or medium-size river that receives the wastewater (Yanin, 2003b). In this interlink, it is expedient to distinguish between the river–wastewater mixing zone and the pollutant distribution zone as a result of natural migration factors. In turn, the mixing zone consists of upper and lower sections. The upper section is usually a stream that receives wastewater. Here, waste and surface waters are initially mixed, and the qualitative and quantitative parameters of water flow substantially depend on the wastewater input mode and composition. In the lower section, wastewater mixes with river water and the flow characteristics depend on the degree of dilution with natural waters. In the distribution zone, the water flow parameters are mainly determined by natural factors, contributing to dispersion and differentiation of pollutants, transformation of their speciation, and redistribution between the components of the river medium. It is in this zone that technogenic alluvial sedimentation processes actively develop, the main material product of which is technogenic silts.

The SPM concentration (sedimentary material) in the water mass can be considered a variable that exists and continuously varies with time—in a dynamic (time) observation series. The accuracy of estimates from studying such series in the general case depends not only on the number of observations, but also on the internal structure of the series (Kendall, 1981). Therefore, in order to study the behavior of solid SPM in river water, it is feasible to conduct observations to establish the time distribution of solid SPM by means of water sampling studies during certain and sufficiently long time periods in areas within the main zones of the above-mentioned interlink, as well as in a background area (a watercourse not subjected to direct technogenic impact). Let us consider the results of such studies performed on the Pakhra River in Podolsk's zone of influence (Yanin, 1984, 2003b, 2013b, 2017a). Here, during the summer low water period, (from July 15 to August 15, i.e., 32 consecutive days), water sampling was carried out daily on three dynamic observation transects and 12 hydrochemical monitoring transects (Fig. 9).

Transect I was located at the mouth of Cherny Creek, the flow of which was almost completely formed by wastewater from Podolsk treatment plants. Observations at this transect make it possible to characterize the delivery of solid SPM to a pollution source and identify the peculiarities of its behavior within the upper part of the mixing zone. Transect II, corresponding to the closing transect of the lower section of the mixing zone, was located on the Pakhra River 2 km below the mouth of Cherny Creek. In this segment, river and wastewaters mix and the SPM distribution is governed by the hydrodynamic processes of dilution with river water.

Transect III was located on the Pakhra River within the distribution zone (9 km below the mouth of Cherny Creek); the area of the river channel before this transect is characterized by a geomorphological structure typical of small lowland rivers; SPM redistribution processes actively occur, a significant mass of them settle here, which leads to the formation of technogenic silts on the riverbed. Transect IV was chosen as the background; it is located on the Moscow River beyond the direct technogenic impact zone (above the Mozhaisk Reservoir). Here, samples were collected in the same time period, but at an interval of three days. Water samples (5 L) were collected in white plastic canisters at the midstream of the watercourse. The SPM content in river water was determined gravimetrically in a field laboratory. In particular, SPM was separated by filtering samples (up to 2 L) under vacuum through membrane nitrocellulose filters with a pore diameter of 0.45 μm, which were preboiled in distilled water, then dried in a desiccator to a constant weight and weighed on an analytical balance. After filtration, the filters with precipitate were dried at room temperature and weighed again. The amount of SPM

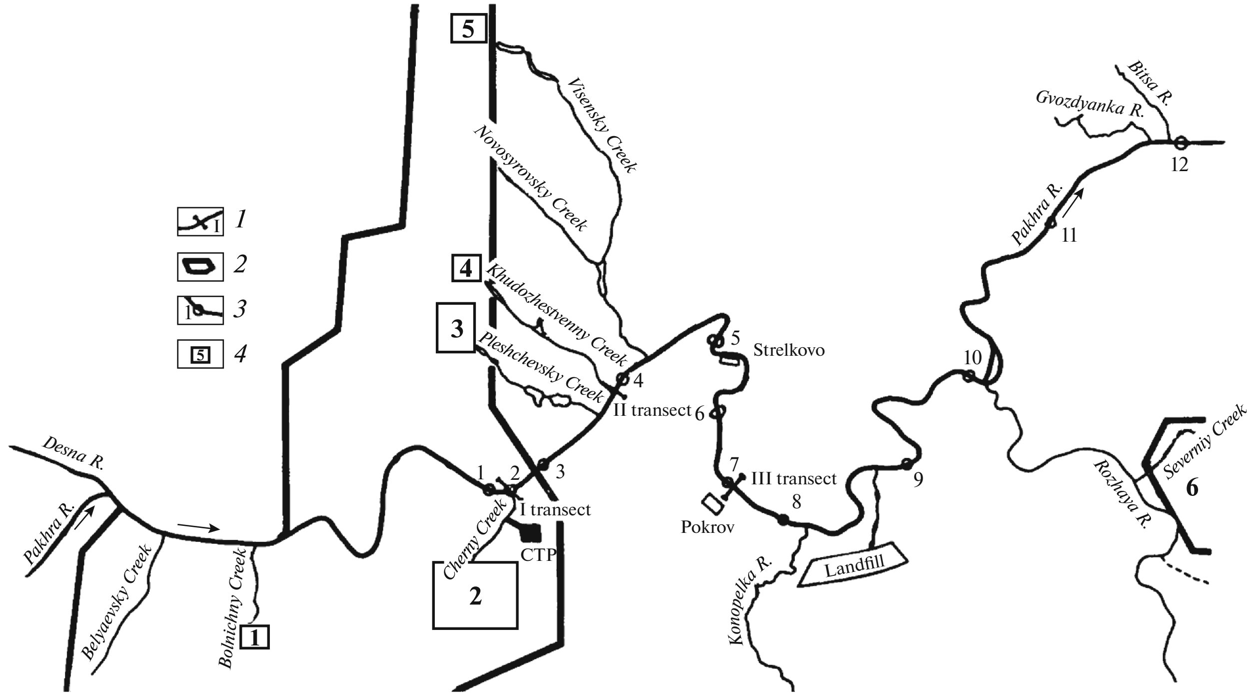

Fig. 9. Scheme of Podolsk environs: *1*, areas of dynamic observations (I, II, III); *2*, boundary of urban area; *3*, areas of hydrochemical monitoring (1–12); *4*, main industrial zones within Podolsk (1–4); town of Shcherbinka (5) and Domodedovo (6).

in the test sample was calculated from the difference in filter mass before and after filtration.

Zonal SPM content values in river water (based on long-term data) from the studied region (the Moscow River basin) in spring are 50–100; in summer–autumn, 10–25; and in winter, up to 10 mg/L (Resursy..., 1973a).

Table 19 shows the characteristics of the SPM distribution in Pakhra River water (transects I–III) and on the background transect (Moscow River). In the background conditions, SPM in the studied period (summer low water) differed by a uniform time distribution ($V = 51\%$), with 90% of samples characterized by SPM concentrations whose scatter fit the standard deviation of the sampling. The maximum SPM concentration (48.8 mg/L) was observed in a period of short-term but intense rain, which increased sediment supply to the river flow from the catchment area; it was accompanied by increased water flow in the river and contributed to the spreading of channel sediments. Overall, for the entire series of dynamic observations, a direct correlation between the specific SPM content in water and water discharge in the river ($r = 0.69$, with a confidence interval of the correlation coefficient of ±0.62 for a 5% significance level) was recorded on the background transect. Thus, in the background conditions, the behavior of SPM is controlled by hydrometeorological factors and its average concentration correlates with the zonal values during summer low water.

Under technogenic pollution conditions, the distribution of SPM concentrations in the dynamic observation range has a nonuniform (discrete) character (Table 19, Fig. 10). This is especially pronounced within the upper part of the mixing zone (transect I), which is confirmed by high values of the variation coefficient, calculated from the standard

Table 19. SPM content in river water on different transects, mg/L

Transect	Mean and its error	Interval	V*	R**	K_C	
					average	maximum
IV (background)	24.16 ± 4.11	6.50–48.80	51	175	–	–
I	53.43 ± 8.68	18.70–288.60	92	505	2.2	11.9
II	27.97 ± 3.07	7.20–82.50	62	269	1.2	3.4
III	26.90 ± 2.81	9.60–83.0	59	273	1.1	3.4

* Variation coefficient for standard deviation; ** variation coefficient for variation range.

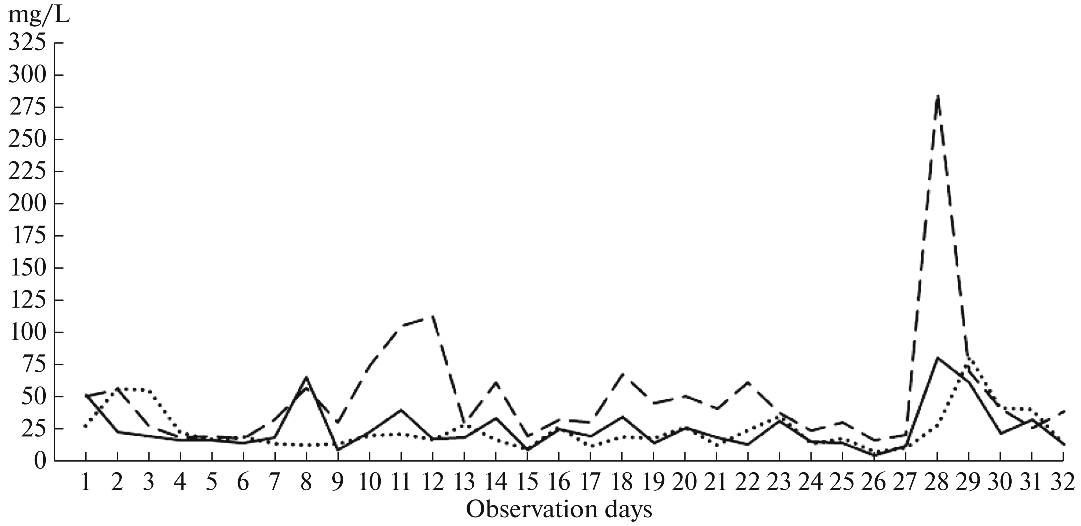

Fig. 10. Distribution of SPM at transects I (dotted line), II (solid line), and III (points).

deviation ($V = 92\%$) and variation range ($R = 505\%$). There was hardly any correlation between the SPM concentrations and their volume in discharged wastewater. This indicates that the temporal nature of the SPM distribution primarily depends on the specifics of how city treatment plants function (i.e., on the degree of wastewater treatment). The average specific SPM concentration on transect I appreciably (by 2.2 times) exceeds the background value. Peak SPM concentrations that significantly exceed the background content is typical. Thus, the technogenic delivery of SPM has a discrete nature and occurs in volumes exceeding the zonal runoff modulus.

Within the closing transect of the lower part of the mixing zone (transect II), the SPM behavior primarily depends on hydrodynamic factors that determine the dilution ratio of incoming wastewater enriched in SPM and river water, the turbidity of which in the area of the channel is higher than that at the mouth of Cherny Creek, 10–15 mg/L.

Naturally, in addition to physical (mechanical) dilution, accelerated sedimentation of coarse-grained SPM with a higher hydraulic velocity is significant, which is a consequence of sewage flow and, accordingly, the decrease in its flow velocity. On the one hand, this leads to a significant decrease in the average specific SPM concentration on transect II, and on the other hand, a decrease in the variation of its content in the observed time series ($V = 62\%$, $R = 269\%$). However, the time distribution of SPM and its concentration on this transect appreciably differ from the background characteristics. In addition, there is no correlation between turbidity and water discharge on transect II ($r = 0.01$, with a confidence interval of the correlation coefficient of ±0.4 for a 5% significance level), and the character of the distribution plot of SPM concentrations on transect II is identical to that of transect I. This demonstrates the leading role of solid technogenic material supply to the water turbidity regime within the lower area of the mixing zone. On transect III, i.e., within the zone of pollutant distribution via natural migration factors, the character of the SPM behavior and levels are in many ways similar to those in the previous area of the river. Nevertheless, there is already a weak correlation between its content in water and water discharge ($r = 0.24$, with a confidence interval of ±0.34 for a 5% significance level), which may indicate secondary SPM delivery, primarily from bottom sediments during the spreading process.

For the SPM distribution in the dynamic observation series on transects I–III, a certain type of systematic effect is recorded, manifested as a certain cyclicity, when peaks (corresponding to maximum concentrations) and valleys (corresponding to minimum concentrations) appear on the plots after a certain time interval (in our case, usually one day). Such time series are called cyclic series (Kendal, 1981). Using the method proposed by M. Kendall (1981) for calculating turning points (on content distribution plots) as a criterion for testing the hypothesis on the randomness of fluctuations with an alternative hypothesis on the presence of systematic fluctuations showed that, basically, the time series of the SPM concentration distribution observed on transects I–III are series of random fluctuations essentially governed by external factors. In this case, the main factor is undoubtedly the regime of sediment transported to the Pakhra River with runoff via Cherny Creek, or rather, the discreteness of sedimentary material delivered with it. Thus, there is a direct correlation between the turbidity distribution series on transects I and II ($r = 0.69$), on transects I and III ($r = 0.41$), and on transects II and III ($r = 0.42$). Determination of the closeness of the linear relationship between this feature (in this case,

Table 20. Chemical composition of SPM, technogenic silts (TS), and background alluvium (BA), %

Component	SPM		TI, Pakhra River, 9 km below Podolsk	BA, Pakhra River	SPM of rivers in the temperate and cold zones, average (Martin and Meybeck, 1978)	SPM of rivers of world, average (Gordeev and Lisitzin, 1978)
	transect I	transect III				
SiO_2	28.3	67.74	61.70	78.50	62.87	54.80
TiO_2	0.40	0.67	0.38	0.48	0.82	0.67
Al_2O_3	5.50	9.47	8.63	4.52	13.58	15.65
$Fe_2O_3 + FeO$	7.36	4.33	4.90	2.62	–	–
Fe_2O_3	–	–	–	–	6.40	7.28
MgO	2.32	1.84	0.66	1.26	2	2.07
CaO	8.14	3.90	6.08	3.17	6	3.52
Na_2O	0.88	0.80	0.68	0.72	1.16	1.35
K_2O	1.15	2.13	1.62	1.60	2.73	1.81
LOI	41.00	8.00	10.88	2.16	–	–

the turbidity distribution on transect III) and two factorial features (water turbidity on transects I and II) showed a high correlation ($r3/1.2 = 0.58$). Thus, in contrast to the background conditions, where the main external factors determining SPM behavior in river water are hydrometeorological phenomena, their role is less significant in the polluted zone. The presence of such cyclicity in the SPM distribution is largely governed by the discrete mode of their supply with runoff discharged along Cherny Creek.

Sedimentary material arriving with sewage plays an important role in forming technogenic pollution zones in the river. According to (Makkaveev and Chalov, 1986), the river flow and its channel in certain periods can be considered a dynamically equilibrium system. However, the supply of significant amounts of solids into the river in the city's zone of influence periodically causes a significant increase in water flow turbidity and SPM overload, which ultimately violates the dynamics of equilibrium exchange of sedimentary material between the water flow and the channel. As a result, in certain parts of the river, especially in the impact zone nearest to technogenic pollution sources (cities), its sedimentation processes begin to predominate, which leads to the formation of technogenic silts (Table 20).

At the mouth of Cherny Creek, sediment formation is largely due to the hydraulic deposition of incoming technogenic sedimentary material, which is associated with a decrease in the flow velocity of runoff, because it is backed up by river water. In the grain size distribution of sewage sludge (SS), in Podolsk, the coarse-grained silt fraction dominates (0.10–0.01 mm); therefore, its content in technogenic SPM is also high, which is reflected in the grain size distribution of channel sediment in the mouth zone of Cherny Creek, characterized by high contents of this fraction. In the area of the Pakhra River below the mouth of Cherny Creek, an active accumulation zone of technogenic silts has been observed, characterized by a decreased share of coarse-grained sand (up to 6.7% vs. 17.6–28.5% in previous areas) and an appreciable increase in the number of silt and clay particles. It has been established that Podolsk SS is distinguished by a high clay content (<0.005 mm) and particularly small silt particles (0.10–0.01 mm), which are obviously present in elevated amounts in discharged wastewater. All this determines the increased content of the silt and clay fractions in the silts formed in this area of the riverbed.

SPM transported with water runoff is characterized by heavy metal concentrations significantly exceeding their background levels (Table 21) and global and regional distribution parameters (Table 22).

In the dynamic observation series, the specific distribution of metals in SPM is characterized by high variability, which is especially pronounced in the river–wastewater mixing zone (Fig. 11). Downstream from the pollution source, for almost all metals, the changes in their concentrations in SPM are similar. The greatest decrease in metal levels in SPM occurs in the first 8–10 km below the transect of complete river–wastewater mixing. Obviously, it is here that technogenic SPM removal from the flow and entry of natural lithogenic particles into the water column are especially active, since the turbidity of river water as a whole changes weakly downstream. Downstream, the gross metal concentrations in SPM decrease in value, often to their background levels.

Heavy metals in sewage-transported technogenic SPM demonstrate significant quantities of their highly mobile (sorption–carbonate) and relatively mobile (organic and oxide) species (Table 23). The metal spe-

Table 21. Heavy metals in SPM

Metal	Average and its error, mg/kg	V*	R**	K_C
Transect I				
Cr	687.79 ± 123.89	52	320	2.2
Ni	556.59 ± 90.34	47	240	4.8
Cu	1587.60 ± 346.90	63	352	8.8
Zn	1637.00 ± 317.80	56	338	2.6
Cd	74.13 ± 16.18	63	313	9.9
Hg	11.56 ± 2.71	68	214	170
Pb	887.13 ± 177.90	58	337	3.4
Transect II				
Cr	497.50 ± 134.90	78	342	1.6
Ni	302.20 ± 83.50	80	284	2.6
Cu	773.03 ± 272.62	102	465	4.3
Zn	1173.50 ± 247.40	61	569	1.9
Cd	34.31 ± 11.82	99	539	4.6
Hg	3.36 ± 1.32	114	470	49.4
Pb	630.70 ± 26.55	122	672	2.4
Transect III				
Cr	451.70 ± 101.80	65	272	1.5
Ni	225.30 ± 36.80	47	239	1.9
Cu	501.70 ± 88.68	51	196	2.8
Zn	922.60 ± 174.30	55	220	1.5
Cd	25.47 ± 7.00	79	393	3.4
Hg	1.74 ± 0.89	148	800	25.6
Pb	378.60 ± 74.62	57	226	1.5

*Variation coefficient for standard deviation, %; ** variation coefficient for variation range, %.

ciation ratio in SPM is characterized by temporal inhomogeneity (Fig. 12). As sedimentary material migrates in a river, the metal speciation balance changes due to various intrawaterbody processes (along with a decrease in concentrations).

Thus, during summer low water in natural conditions, SPM in river water is distinguished by a uniform time distribution, their behavior is controlled mainly by hydrometeorological factors, and the average specific SPM concentration correlates with zonal indicators. Technogenic sediment supply has a discrete time character and occurs in quantities exceeding the zonal flow modulus. The participation of significant masses of technogenic material in sedimentogenesis is reflected in the sediment flow regime and alluvial sedimentation processes. The features of the SPM distribution in the dynamic observation range, manifested as highly variable concentrations, are determined by the operational specifics of the sewage treatment plant, the discrete mode of sediment input with wastewater, the dilution rate of the latter by river water, and accelerated coarse-grained sedimentation processes. Sedimentary material entering the river with sewage is characterized by a specific petrochemical composition, high concentrations of many chemical elements, significant quantities of their geochemically mobile forms, and its active involvement in alluvial sedimentation processes.

MORPHOLOGICAL FEATURES AND MATERIAL COMPOSITION OF TECHNOGENIC SILTS

Technogenic silts are common in the channels of many (especially small and medium-sized) rivers in economically developed areas. They are characterized by a peculiar morphological appearance and participate in the formation of the channel relief. The grain-size distribution, mineral composition, and petrochemical characteristics of technogenic silts fundamentally distinguish them from typical natural (background) channel alluvium. The uniqueness of such silts as a new variety of modern alluvial sediments is also manifested in the group structure and composition of organic matter peculiar to them and in the wide distribution of their artificial particles.

Morphology and Structure of Technogenic Silts

Technogenic silts are dark gray or black, sometimes interlayered with ash-colored sediment, soft on top

Table 22. Heavy metals in technogenic SPM (TSPM) and solid SPM of rivers

Metal, mg/kg	TSPM, transect I	Rivers of world				Rivers of Europe (Viers et al., 2009)
		(Martin and Meybeck, 1979)	(Viers et al., 2009)	(Savenko, 2006)	(Gordeev and Lisitzin, 1978)	
Cr	687.79	100	130	85	130	164
Ni	556.59	90	74.5	50	84	66
Cu	1587.60	100	75.9	45	80	172
Zn	1637.00	250	208	130	31	346
Cd	74.13	–	1.55	0.5	0.7	–
Hg	11.56	–	–	0.077	–	–
Pb	887.13	100	61.1	25	147	71

(often in the form of a peculiar saturated suspension), denser and more plastic, with an unpleasant smell downsection (fecal, chemical, and sometimes in their lower layers, a faint odor identified as hydrogen sulfide), slick and oily to the touch (Yanin, 1989, 2002c, 2004a). Often the silt sequence is interlayered with gray or black sand. The silts leave a stain; prolonged contact irritates the skin and has a corrosive effect on rubber (gloves, boots, boats). The vertical thickness of silts widespread in streams and small and medium-sized rivers varies from a few centimeters to 3–3.5 m. A special variety of silts is oozy sediments (up to 1–3 cm thick) that form on point bars. In their main mass, silts are sticky and plastic, which indicates the presence of significant molecular attraction forces between constituent particles, which in turn determine the cohesion and increased stability of sediments to the eroding action of water flow, as well as the low filtration rate through their (especially lower) sequence. As a rule, silts recovered with a corer retain their structure, and when dried, retain their shape. The stickiness and plasticity contributing to increased cohesion of the main mass of silts are largely related to colloidal films, various organic substances (petroleum products, synthetic oils, PAHs and their derivatives, synthetic surfactants, etc.), as well as fibrous particles. Stirring up of silts is accompanied by gas seeps and the appearance of iridescent, oily spots and films on the water

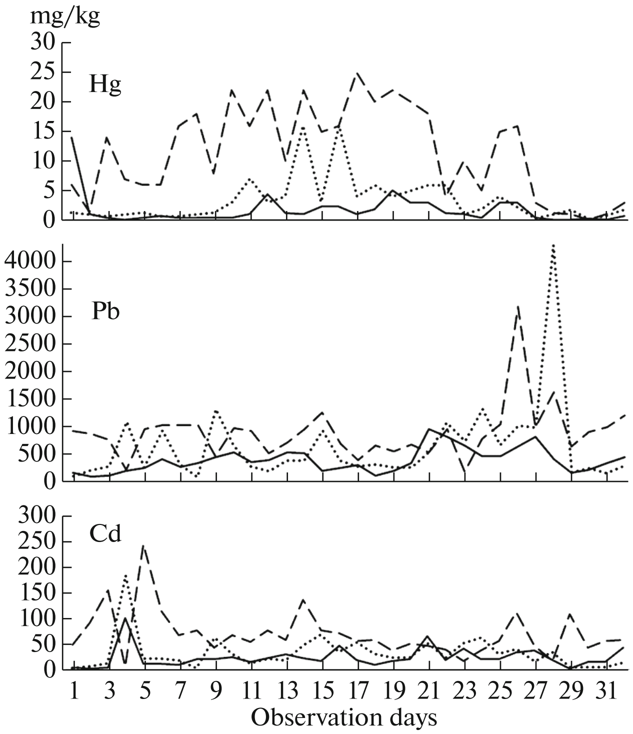

Fig. 11. Distribution of specific concentrations of heavy metals in SPM at transects I (dashed), II (points), and III (solid line).

Table 23. Heavy metal speciation in SPM*

Transect	Gross, mg/kg	Sorbate–carbonate		Organic		Oxide		Crystalline		Silicate	
		1**	2***	1	2	1	2	1	2	1	2
					Nickel						
I	425	172.1	40.5	63.3	14.9	65.5	14.7	54.4	12.8	72.7	17.1
II	258	112.0	43.4	37.2	14.4	38.2	14.9	57.3	22.2	13.3	5.2
III	156	80.8	51.8	18.9	12.1	13.1	8.4	32.0	20.5	11.2	7.2
Background	40	21.0	52.5	5.0	12.5	0.8	2.0	6.7	16.7	6.5	16.3
					Copper						
I	1386	43	3.1	223.2	16.1	313.2	22.6	731.8	52.8	74.8	5.4
II	747	139.7	18.7	171.1	22.9	221.1	29.6	183.0	24.5	32.1	4.3
III	520	122.2	23.5	147.2	28.3	125.2	24.1	110.8	21.3	14.6	2.8
Background	50	15.2	30.3	20.1	40.3	6.1	12.3	8.0	16.0	0.6	1.1
					Cadmium						
I	78.3	57.1	72.9	2.7	3.5	10.3	13.1	4.8	5.2	3.4	4.3
II	40.0	33.4	83.5	0.6	1.5	4.3	10.8	0.6	1.5	1.1	2.7
III	30.0	25.2	83.8	0.3	1.1	3.8	12.7	0.3	1.1	0.4	1.3
Background	0.65	0.085	13.1	0.247	39.0	0.082	12.5	0.11	16.9	0.126	19.5
					Lead						
I	1023	81.8	8	68.6	6.7	308.9	30.2	509.5	49.8	54.2	5.3
II	670	79.1	11.8	71.0	10.6	188.9	28.2	253.3	37.8	77.7	11.6
III	280	45.4	16.2	57.7	20.6	84.8	30.3	82.9	29.6	9.2	3.3
Background	70	8.48	12.1	2.1	3.0	17.0	24.3	29.62	42.3	12.80	18.3

* Average values for the 30-day period are given; ** specific concentration, mg/kg; *** share of form out of gross, %.

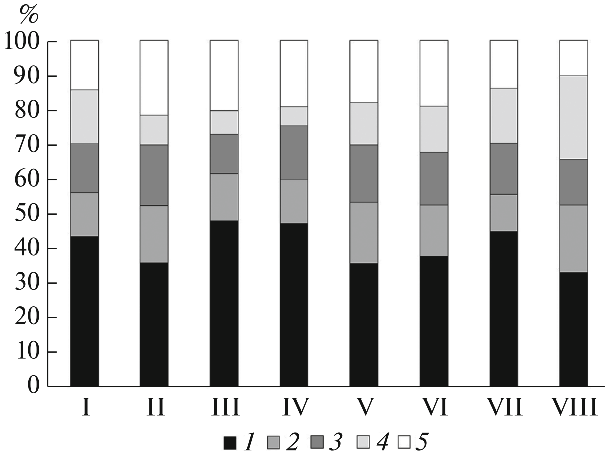

Fig. 12. Balance of nickel speciation in SPM, transect I. Forms: (*1*) sorption–carbonate; (*2*) organomineral; (*3*) oxide; (*4*) crystalline; (*5*) silicate; I, II, III, etc., are averaged samples (each sample of separation suspension combines samples for 3–4 observation days).

surface; the Tyndall effect (milkiness) is observed in a glass container of such water after it settles.

In areas with maximum accumulation, silts, as a rule, demonstrate a certain stratification. The upper layer (~0–20 cm) most often consists of a flocculent suspension (a saturated colloidal solution, a hydrosol), sometimes a free-flowing mass of organomineral composition, a peculiar mixture of mineral and organic SPM, hydrolysates, oxidates, etc. Since the fluid volume confined to this layer often exceeds the volume of solid material, such a formation can be called a coagel. The formation of such a layer leads to an indistinct interface between the water flow and sediments proper. Apparently, it is in this layer that, e.g., amorphous metal hydroxides and various complexes coagulate and form, in which newly deposited matter and entrained sediments are relatively firmly trapped by the coagel structure. Here, of course, sorption processes actively occur, which increases the oxidation rate of organic matter. The constant supply of flow-transported SPM into the layer, including as a result of colmation, reduces its kinetic (sedimentation) stability, leads to the development of adhesion and spontaneous consolidation of particles, settling of even very fine particles, and, as a result, further aggregation and binding of accumulated silt sediments in the river channel. In particular, according to (Mirtskhulava, 1988), the presence of fine-grained SPM in the water flow (typical of urban rivers) clogs the bottom of the channel, as a result of which bottom sediments become cohesive and erode only at very high flow velocities. In addition, the presence of fine-grained SPM in the flow reduces hydraulic resistance and flow turbulence (Voitinskaya, 1973), which also increases the erosion resistance of the resulting technogenic silts. The delivery of fine-grained particles into the upper layer of silts is also facilitated by the existence of the so-called viscous water-flow sublayer (Borovkov, 1989), within which movement rates are relatively small and the particle size of the suspension is less than the thickness of this sublayer. Also important are surface cohesive forces occurring due to small settling particles that approach the denser lower silt layers, making it difficult for solid particles to rerise. In the next silt layer (~20 to ~ 60 cm), viscosity increases, porosity decreases, and solid matter prevails over the fluid. However, the presence of sufficient water in silts still prevents individual particles from contacting. Here, silts form with a peculiar cellular–flocculent (porridgelike) structure and, as a rule, viscous consistency. Even lower, in the 60–70 to 100–120-cm layer, less hydrated, more aggregated and denser silts are traced, mostly with a sticky-plastic consistency. In the lowest silt layers (110–120 to 300–350 cm), largely due to gravitational compaction; loss of free, loosely bound, and partly colloid-bound water; and a decrease in organic matter content—the porosity of sediments markedly decreases; particles are rearranged in the structure of silts and the number of contacts increases between solid particles, which are able to combine into larger aggregates, as a result of which sediments become denser and acquire a viscoplastic consistency. The solid phase of silts already predominates over the liquid. It cannot be excluded that progressive gravitational compaction of silts eventually immobilizes part of the free water, which becomes colloid-bound.

Technogenic silts are widespread in the rivers of the studied industrial–urbanized areas, particularly in the Moscow River and its tributaries within and below the city of Moscow, in the Pakhra River and its tributaries (Fig. 13), in the Klyazma River and its tributaries, and in the beds of other rivers and streams that receive and collect wastewater and surface runoff from developed territories (Yanin, 2002b, 2004a). The intensity of technogenic sedimentary material supplied to rivers can be so significant that silts form even within dynamic areas of urban wastewater discharge into rivers (Fig. 14).

In Mordovia, within areas of the river network located outside direct technogenic impact zones, riverbeds also consist mainly of sandy sediments. For example, channel sediments widespread in the upper reaches of the Insar River are represented by coarse- and medium-grained sand with an abundance of gravel, pebbles, sometimes grus and gravel, and a slight admixture of clay particles (Yanin, 2002c, 2007c).

In zones of influence of cities and towns, watercourses are rife with technogenic silts. Thus, they cover a significant part of the bed of the Insar and its tributaries (the Lepeleyka River, Nikitinsky Creek, the Saranka River, etc.) that drain the city of Saransk and its environs. Within the urban part of the hydrological network, the vertical thickness of silts varies from 0.2–

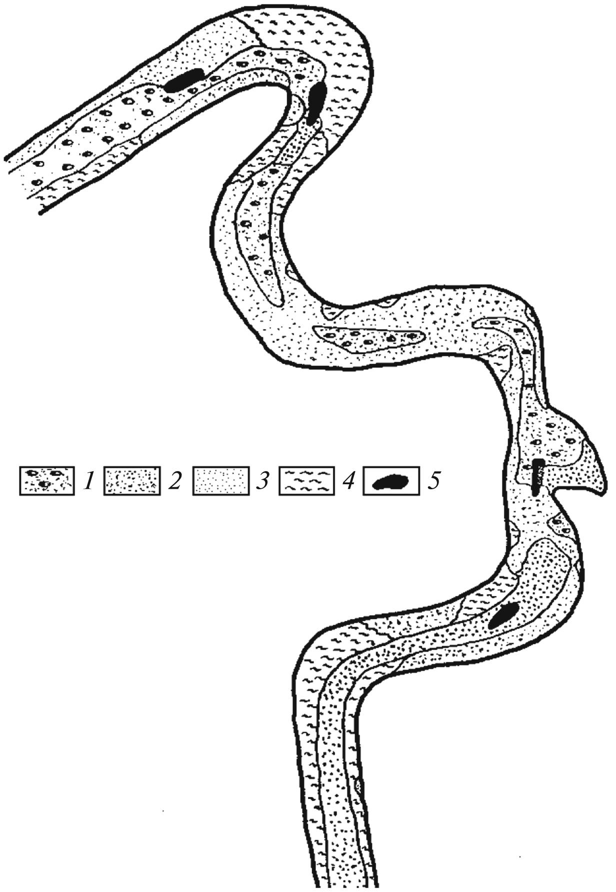

Fig. 13. Lithological diagram of Pakhra River 9 km below Podolsk. Here and in Fig. 14: (*1*) gravel–pebble sediments with sand aggregate; (*2*) coarse-grained sand; (*3*) fine-grained silty sands; (*4*) technogenic silts; (*5*) islands.

0.3 to 1–1.2 m. Below areas of wastewater discharge from Saransk treatment plants, silts make up almost the entire Insar riverbed, and their thickness in some areas reaches 2–3.5 m. Usually, the maximum accumulations of technogenic silts are observed on the banks (Fig. 15); the midstream parts of the channel, as a rule, are covered with variously grained sand with pebbles, cobbles, gravel, and grus, but with an abundance of silt particles acting as a kind of filler in the main sediment sequence.

Silt accumulations (up to 1.2–1.5 m) in the form of relatively large lenses and ridged formations can be traced to the mouth of Insar River; silts form point bars (such as shoals) and small braid bars, accumulate in floodplains and reach hollows on a low floodplain, especially when thickets of both macrophytes and terrestrial plants develop on it. Sometimes silts with a layer of up to 2–3 cm cover morphologically well-expressed sandbanks. At the mouth of the Insar, they form point bars, as well as a delta, where their thickness reaches 1–1.2 m. The volume of technogenic silts in the Insar River channel is estimated at 0.8–0.9 million m^3. The silts are widespread (in bars, along banks, in backwaters, in macrophyte thickets) and in the Alatyr River channel, into which Insar flows; silt accumulation in the Alatyr goes even 50–70 km lower than the mouth of the Insar. Here, they are traced in the form of lenticular clusters with a thickness of up to 0.8–1.2 m near banks, covering large parts of the riverbed (up to the 20–30 cm layer) or point bars; they are encountered within the midstream areas of the channel and are a filler in sand–gravel sediments.

Of particular interest is material obtained on the Nura River in the zone of influence of Temirtau, where technogenic silts are most widespread in the river channel and valley and determine to a large extent the extreme ecological situation there owing to intense mercury pollution, the main concentrator and carrier of which are silts (Yanin, 1989, 1992, 2004b).

The background areas of the Nura River channel are covered by typical channel alluvium, which consists of a variety of sands mainly with a quartz composition. Within and below Temirtau (below the dam of the Samarkand Reservoir), the riverbed is largely, especially in the first 25–30 km, composed of technogenic silts, the vertical thickness of which varies from 0.5–1 to 3–3.5 m (Figs. 16–20). With distance from

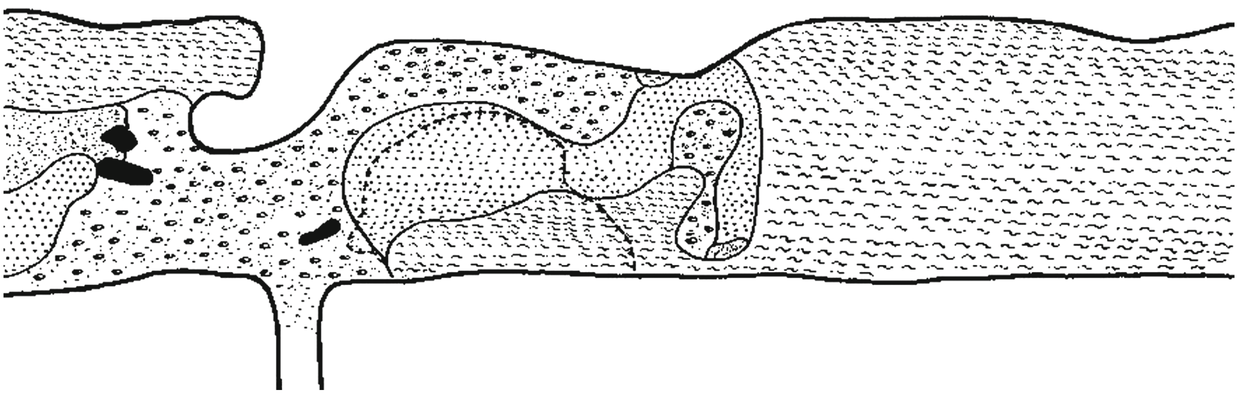

Fig. 14. Lithological diagram of Pakhra River channel at confluence with Cherny Creek, which carries wastewater from Podolsk.

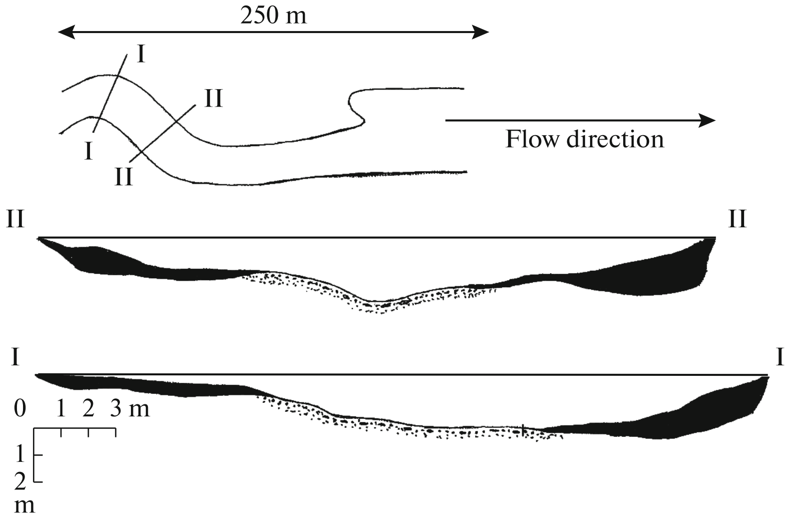

Fig. 15. Cross section of Insar riverbed below city of Saransk: solid dark color, technogenic silt; other, sand-gravel sediments with inclusions of silt particles.

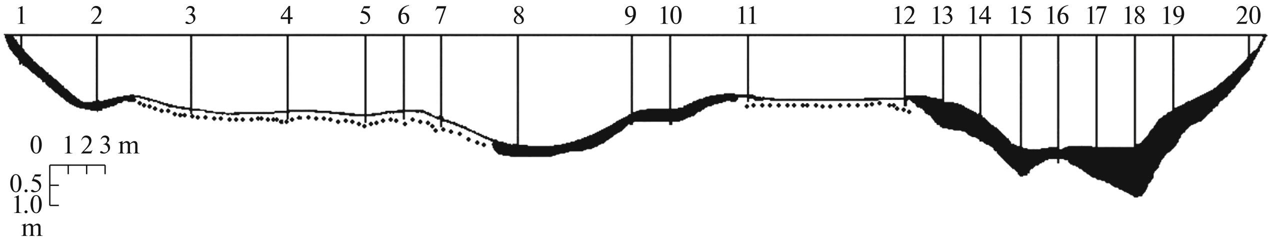

Fig. 16. Cross section of Nura above main wastewater canal (1986 survey). Here and in Figs. 17–20: solid dark color, technogenic silts; other, channel sands and sand–gravel mass with silt particles; Arabic numerals, main sampling verticals.

the city, silts are encountered in the form of accumulations near banks, on bars, in shallows, in backwaters, and distributaries. The silt-free areas of the channel are covered with sandy–gravel–pebble material and sands of various grain size in which silt particles are present. Sometimes silts form significant accumulations even 80–100 km from the city, completely covering the riverbed with a thickness of 40–50 cm, e.g., in the distributaries that function during floods and highwater periods. The volume of technogenic silts in the area of the Nura River (for an extent of 100 km) below Temirtau is estimated at 1.3 million m^3, of which 340000 m^3 is in the first 9–10 km of the channel.

Thus, in rivers of industrial–urbanized territories, a peculiar type of river sediments form: technogenic silts, which differ from background channel alluvium in their morphological appearance and physical properties. The most important properties of silts that demonstrate a certain stratification in places of greatest accumulation resulting from their accumulation conditions and secondary transformations are their dark gray or black color; they have a specific (chemical, fecal, and sometimes hydrogen sulfide) odor, a predominantly viscous or soft-plastic consistency, and high concentrations of fine-grained particles and organic matter. These properties are relatively stable both in the silt sequence, the thickness of which varies from 0.2–0.5 to 2–3.5 m, and over a considerable extent of the channel (many tens of kilometers). Heavy accumulation of technogenic silts is often predetermined by favorable geomorphological conditions (general widening of the river valley, the formation of a wide floodplain channel, the presence of numerous meanders, flattening of the longitudinal profile of the bed), the development of macrophyte thickets and low rates during low-flow periods. A certain role is played by hydraulic engineering structures (dams, bridge crossings, etc.). In the general case, the delivery of significant volumes of technogenic sedimentary material into rivers and subsequent accumulation of technogenic silts in the channel significantly alter the sediment regime and alluvial sedimentation conditions, while influencing the evolution of channel processes.

Grain Size Characteristics of Technogenic Silts

Grain size distribution is an important characteristic of alluvial sediments, since it affects their physical

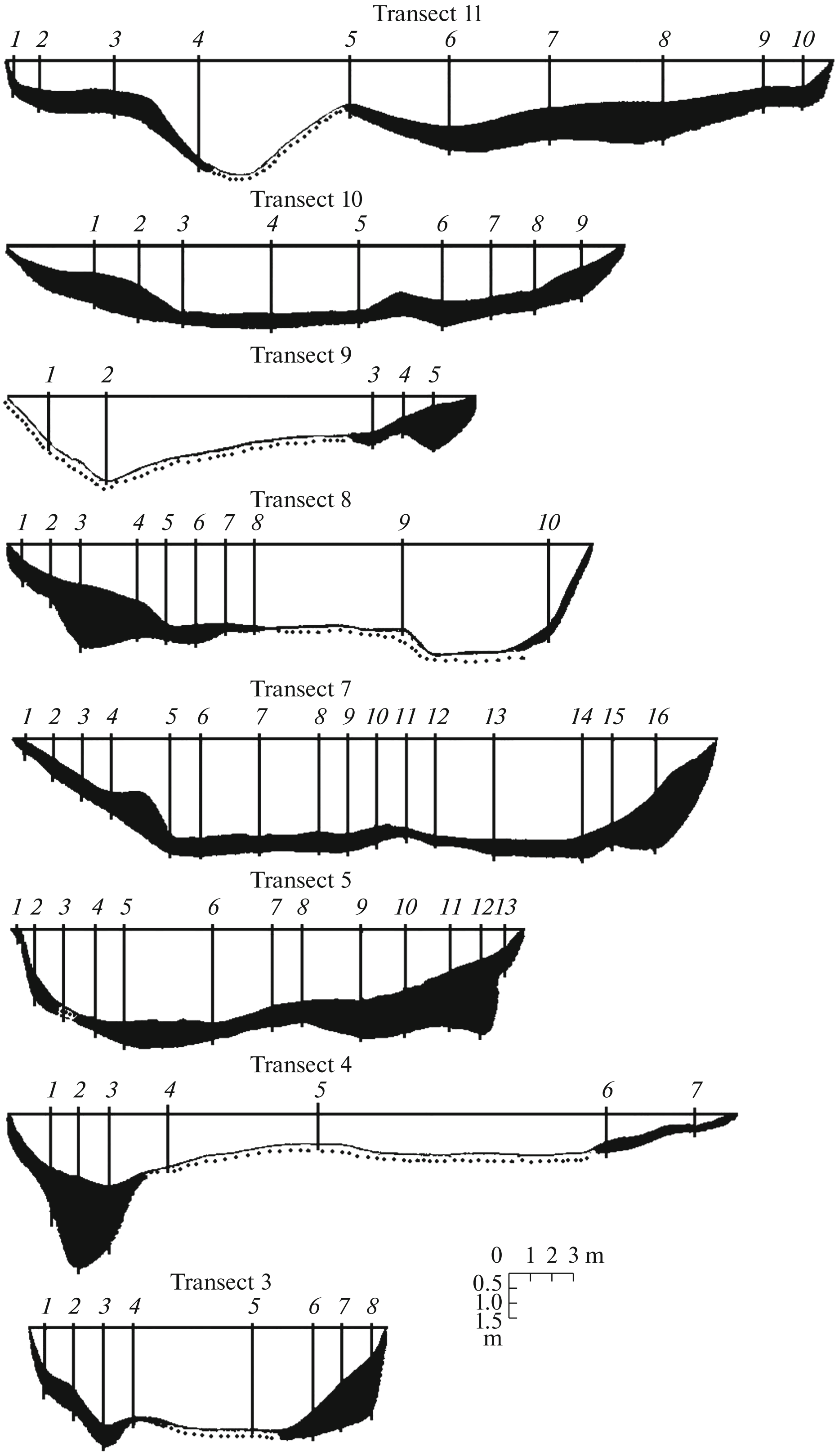

Fig. 17. Cross sections of Nura River channel Location of areas below main wastewater canal (MWC), km: (*3*) 1.1; (*4*) 1.4; (*5*) 2.6; (*7*) 3.2; (*8*) 4.4; (*9*) 5.4; (*10*) 7.1; (*11*) 9.

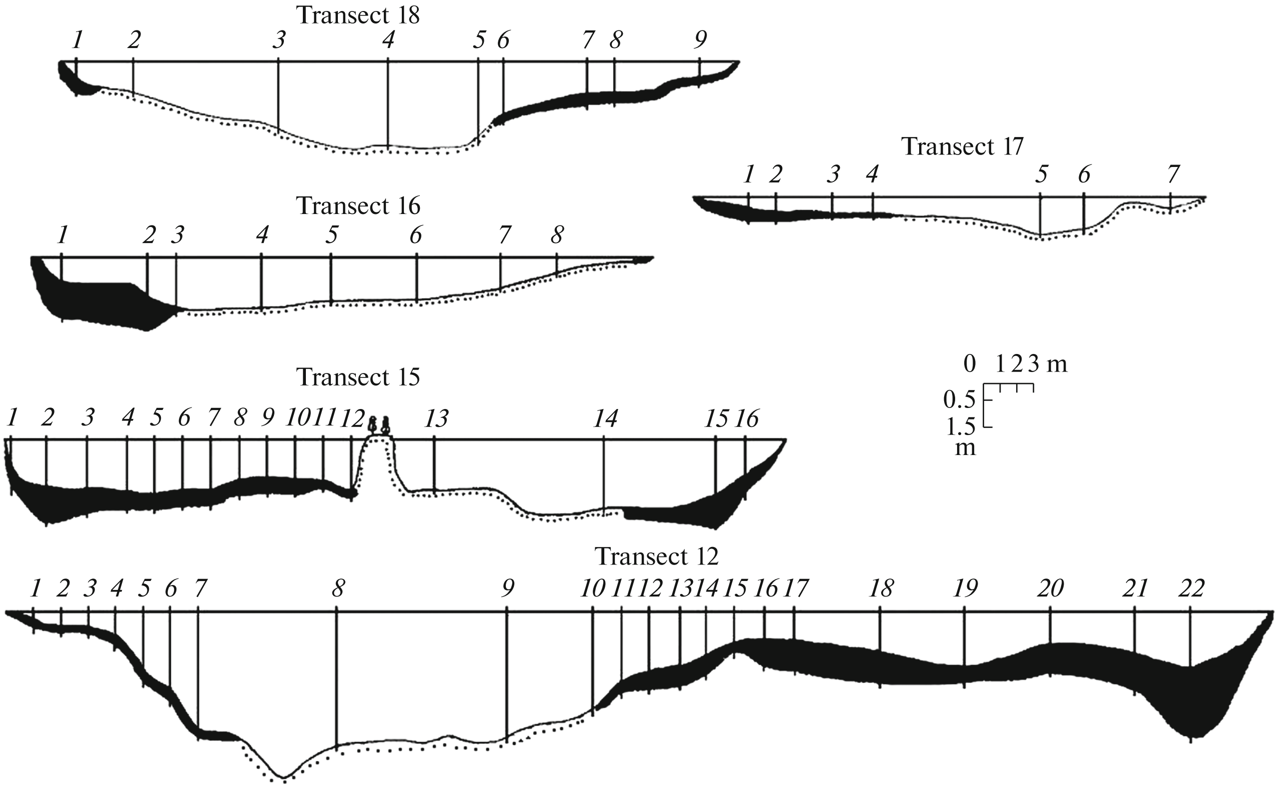

Fig. 18. Cross sections of Nura River channel Location of areas below MWC, km: (*12*) 12.5; (*15*) 20.6; (*16*) 23.8; (*17*) 28.8; (*18*) 31.9.

and chemical properties and mineralogical and geochemical features. The accumulation intensity and distribution features of many pollutants in river sediments and the channel-forming significance of the latter largely depend on the size of particles that form them. Below is a description of the grain size distribution of alluvium and technogenic silts widely encountered in the channels of the Pakhra (Yanin, 2004a, 2009), Insar, Alatyr (Yanin, 2002, 2007), and Nura rivers (Yanin, 1989, 1992).

Moscow region. On the Pakhra River, sediments (layer 0–20 cm) were collected in eight areas (Fig. 21): 1 and 2 km above Podolsk (local background); in the city center; at the mouth of Cherny Creek; and 2, 9, 12 (transect of Shcherbinsky landfill), and 25 km below Cherny Creek.

Samples of sewage sludge (SS) generated at city treatment plants (CTPs) during treatment of Podolsk wastewater, as noted above, being a geochemical analog of technogenic silts, were collected from silt lagoons (10–50 cm layer) located on the right wall of the river valley near the mouth of Cherny Creek. In total, five SS samples (from five silt lagoons) were collected, from which an average sample was formed.

The grain size distribution of background channel alluvium of the Pakhra River is characterized by the following indicators: fine-grained sand fraction, 43.1–47.2%; medium-grained sand fraction, 28.8–29.8%; coarse-grained silt fraction, 18.7–23.2%; there are very few clay particles (0.4–0.6%); and the amount of silt and clay (<0.01 mm fractions) is also small (0.9–1.3%) (Tables 24, 25). It is characteristic that in the moraine sediments and surface clay loams of Moscow oblast, which play an important role in supplying rivers with natural sedimentary material, small- and fine-grained sands and silts are rock-forming sediments (Polyakov, 1956). Thus, the grain size distribution of background alluvium is largely determined by the composition of eroded rocks and reflects the natural differentiation of sedimentary material by channel processes.

In channel sediments widespread in the Pakhra area within the central part of Podolsk (area III), there is a significant (compared with the local background) increase in the share of coarse- and fine-grained silt and clay. The latter, of course, results from the transport of solid material with factory wastewater in the city's central industrial zone. For example, according to (Evilevich and Evilevich, 1988), particles of the 0.1–0.01 mm fraction predominate (>90%) in industrial slurries, which suggests their significant presence in the SPM composition of discharged industrial wastewater.

At the mouth of Cherny Creek (area IV), sediment formation is largely due to the hydraulic deposition of incoming technogenic sedimentary material, which is

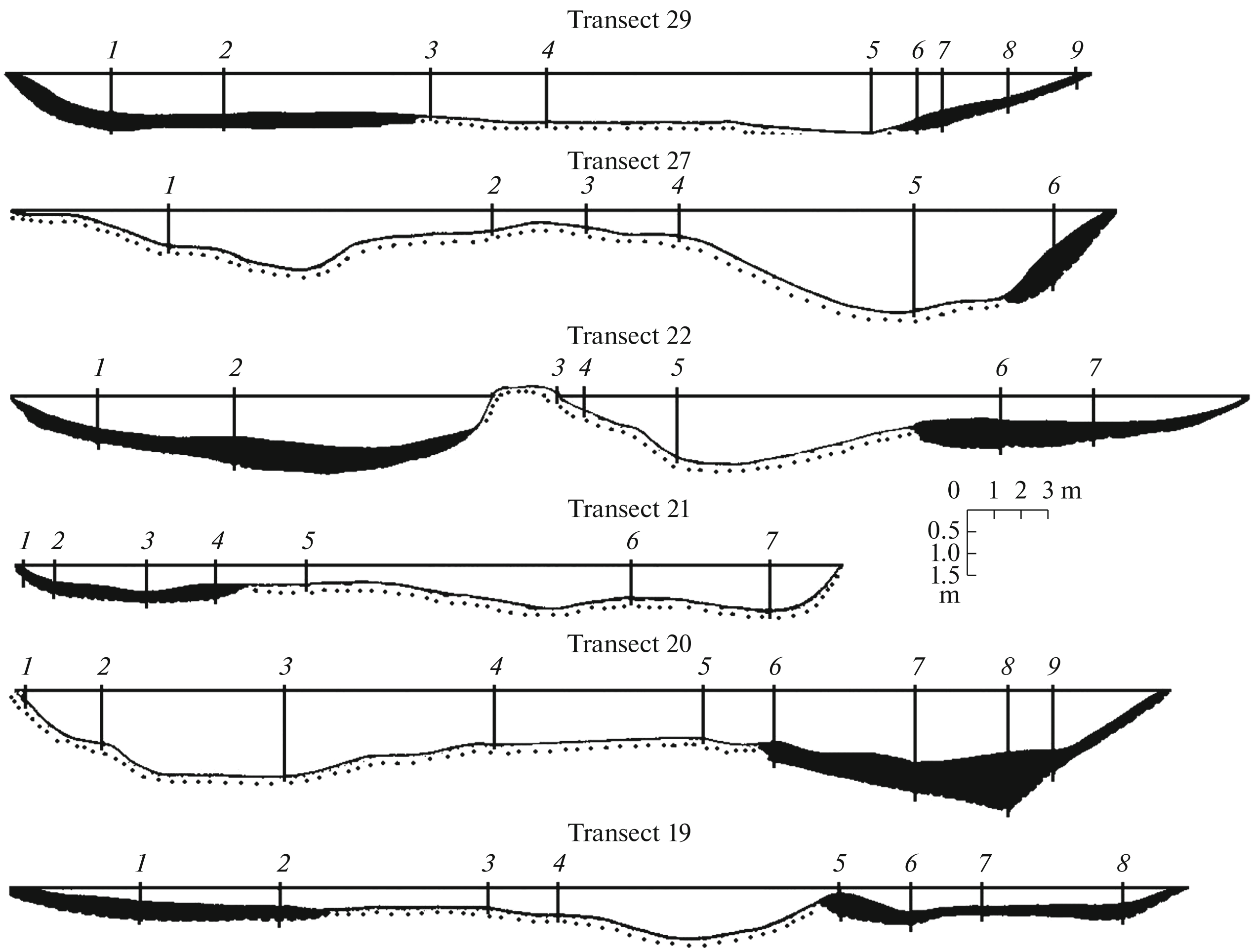

Fig. 19. Cross sections of Nura River channel Location of areas below MWC, km: (*19*) 39.4; (*20*) 44.5; (*21*) 48.2; (*22*) 51.2; (*27*) 61.5; (*29*) 72.5.

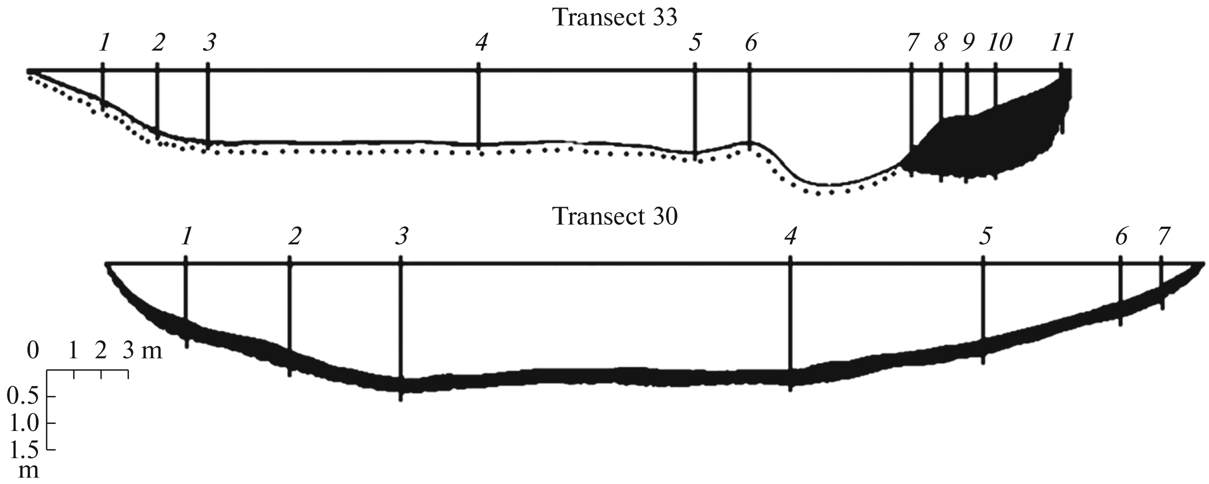

Fig. 20. Cross sections of Nura River channel. Location of areas below MWC, km: (*30*) 90.5; (*33*) 105.5.

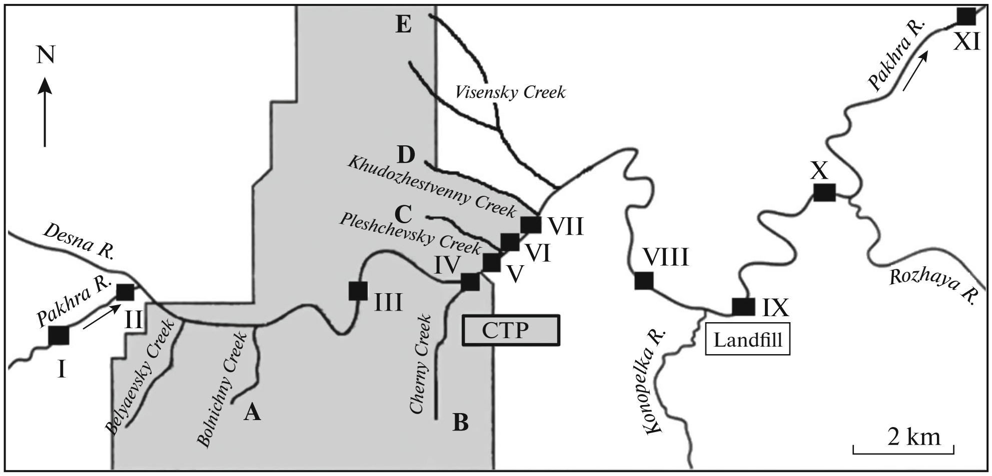

Fig. 21. Channel sediment sampling map of Pakhra River near Podolsk: A–D, main industrial zones; CTP, city treatment plants; Landfill, Shcherbinsky landfill; I–XI, sampling areas: for particle size analysis (I–IV, VII–IX, XI), group composition of organic matter (II, III, V–VIII, X), metal speciation in sediments and silt water (I IV, V, VII, VIII, XI).

related to a decrease in the flow velocity of runoff backed up by river water. According to (Turovsky, 198), the coarse-grained silt fraction dominates in the SS composition (0.10–0.01 mm); therefore, it seems that its content in technogenic SPM is also large, which is reflected in the grain size distribution of sediments in the mouth zone of Cherny Creek, which is characterized by high contents of this fraction. It is indicative that the share of particles corresponding to the silt–clay fraction (<0.01 mm) is also quite large here. Below the mouth of Cherny Creek, an active technogenic silt accumulation zone was observed, characterized by a decreased share of coarse-grained sand (up to 6.7% vs. 17.6–28.5% in previous areas) and an appreciable increase in the number of silt and clay particles. A significant increase in the share of coarse-grained sand in channel sediments in subsequent areas of the Pakhra seems largely due to geomorphological factors contributing to the sedimentation of coarser-grained fractions carried by the water flow (widening of the river valley, flattening of the longitudinal profile of the riverbed, meandering, and the presence of islands). Left bank streams flowing into the Pakhra drain territories where construction and production of building materials were carried out; larger sedimentary material was transported into the river. Nevertheless, the technogenic silts found widely here retain their particular grain size, which differs

Table 24. Grain size distribution of channel sediments of Pakhra River and Podolsk sewage sludge, %

Sampling site (area, see Fig. 21)	Size of fractions, mm						
	>1 (1)	1–0.25 (2)	0.25–0.10 (3)	0.10–0.01 (4)	0.01–0.005 (5)	<0.005 (6)	<0.01 (7)
			Typical channel alluvium (local background)				
Above City (I)	4	28.8	47.2	18.7	0.7	0.6	1.3
″(II)	3	29.8	43.1	23.2	0.5	0.4	0.9
			Technogenic silts (pollution zone)				
City Center (III)	1.5	28.5	32.5	30.2	4.9	2.4	7.3
Cherny Creek mouth (IV)	1.4	17.6	36.3	38.3	4.9	1.5	6.4
2 km below creek (VII)	0.8	6.7	31.3	45.1	8.7	7.4	16.1
9 km″(VIII)	0.5	28.3	30.2	28.8	7.6	4.6	12.2
12 km ″(IX)	0.4	17.1	28.3	43.1	6.8	4.3	11.1
25 km ″(XI)	1.5	15.2	38.2	39.2	3.1	2.8	5.9
			Sewage sludge				
Podolsk	1.7	16.8	8.1	56.7	5.5	11.2	16.7

(1) coarse-grained sand, (2) medium-grained sand, (3) fine-grained sand, (4) coarse-grained silt, (5) fine-grained silt, (6) clay, (7) silt and clay.

from background alluvium by higher contents of fine-grained silt and clay. In the zone of influence of the Shcherbinsky landfill (area IX), the grain size distribution of silts changes mainly due to a decrease in the share of coarse-grained sand and an increase in the content of fine-grained silt, which certainly resulted from the removal of fine soil from the landfill area and intense accumulation of sedimentary material from Podolsk treatment facilities. At the end of this area of the Pakhra, a decrease in the number of fine particles and an increase in the share of fine-grained sand (dominant in background alluvium) are naturally observed in channel sediments, due to the redeposition of technogenic sediments and their blending with natural material. At the same time, the silt–clay content in silts here is significantly higher than in the background alluvium, which emphasizes their lithological nature. The spatial distribution of fine-grained particles (especially silt and clay) in channel sediments clearly localizes the zone of influence of the city (Fig. 22). In terms of sand, silt, and clay, technogenic silts, which differ sharply from background alluvium, are close to SS. This indicates the leading role of wastewater-transported material in their formation (Fig. 23).

The values of the particle size indicators distinctly illustrate the observed differences in the composition of alluvium and silts and the spatial transformation of the latter's grain size distribution. For example, the average (median) diameter Q_{50} of background alluvium in the Pakhra River exceeds 0.1 mm, while the same indicator for silts fluctuates from 0.031 to 0.075 mm. It is typical that the average (median) diameter of alluvium in the rivers of the Smolensk–Moscow upland is on average 0.43 mm (Stok nanosov..., 1977); the median diameter of channel alluvium of the Oka River is 0.33–0.46 mm (Lazarenko, 1964). The mean diameter M_d of background alluvium of the Pakhra River is 0.32–0.33 mm; of industrial sludge, 0.13–0.24 mm. Silts differ from alluvium by higher clay contents. Quantity S_O (particle sorting coefficient), as is well known, admits a certain conditionality (Strakhov et al., 1954). Usually, sediments are considered well sorted when $S_O < 2.5$ and poorly sorted when $S_O > 4.5$. In our case, alluvium is characterized by intermediate sorting, and silts are distinguished by poor sorting.

In accordance with the classifications of sedimentary formations (Strakhov et al., 1954), which are based on median diameter values (after N.M. Strakhov) and the relative clay-and-silt content (after M.V. Klenovaya), the background alluvium of the Pakhra River is typical sand, while technogenic silts are sandy silt or fine-grained silt (less commonly, coarse-grained silt). In general, it can be assumed that the background alluvium is predominantly well-sorted sands of various grain size, characterized as loose soils (Q_{50} is significantly greater than 0.05 mm); technogenic silts are poorly sorted sandy or fine-grained silts, which are cohesive soils (Q_{50} in some cases it does not exceed 0.05 mm, and if greater, it is insignificantly so). The increased cohesion of silts due to the high content of fine-grained particles and organic matter makes these sediments erosion-resistant, which determines their participation in relatively stable forms of the channel relief.

Table 25. Grain size indicators of channel sediments of Pakhra River and Podolsk sewage sludge

Sampling site	Q_{50}	Md	S_O	S_k	K_{cl}
Channel sediments of Pakhra River					
Above city	0.101	0.33	3.8	1.63	0.01
City center	0.075	0.14	8.5	0.95	0.08
Cherny Creek mouth	0.062	0.21	5.2	0.86	0.07
2 km below creek	0.031	0.13	6.1	0.88	0.19
9 km ″	0.069	0.24	9.5	0.79	0.14
12 km ″	0.043	0.18	5.4	0.86	0.13
25 km ″	0.058	0.20	4.0	0.62	0.06
Sewage sludge					
Podolsk	0.080	0.17	2.3	1.16	0.20

Here and below: Q_{50}, median diameter, mm; Md, mean diameter, mm; S_O, particle sorting coefficient; S_c asymmetry coefficient; K_{cl}, clay content ratio (ratio of silt–clay content to amount of other fractions).

Thus, the background areas of the Pakhra River channel are composed of relatively graded, relatively well-sorted sands, which are loose soils, the grain size distribution of which reflects the natural differentiation of sedimentary material coming from the catchment area by channel processes. In the background alluvium, the average (median) particle size of which is ~0.1 mm, the fine- (43.1–47.2%) and medium-grained (28.8–29.8%) sand fractions dominate; the share of clay particles is 0.4–0.6%; the silt–clay content is 0.9 –1.3%. In the zone of influence of Podolsk, where significant masses of technogenic sedimentary

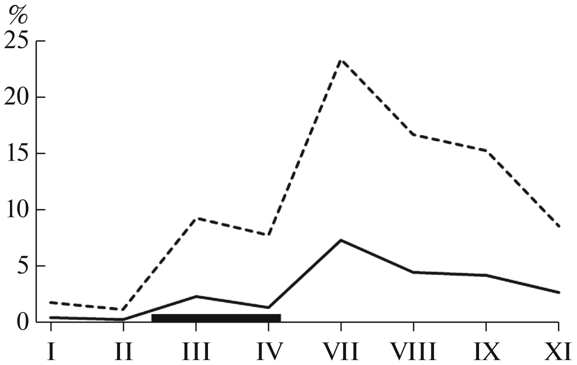

Fig. 22. Distribution of silt–clay (dotted line) and clay fraction (solid line) in channel sediments Pakhra River in zone of influence of Podolsk: I–XI, sediment sampling sites. Dark rectangle, territory of city.

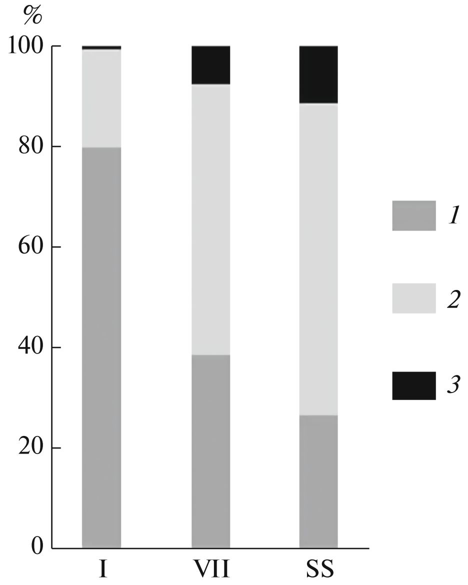

Fig. 23. Ratio of main grain size fractions in background alluvium (area I), technogenic silts (area VII), and sewage sludge (SS): (*1*) sand; (*2*) silt; (*3*) clay.

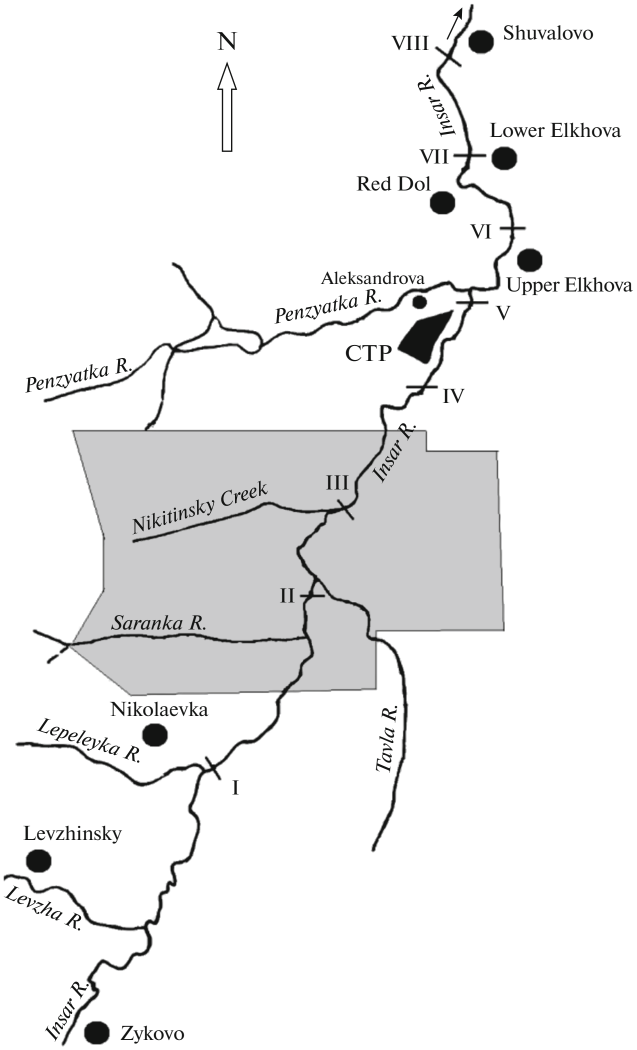

Fig. 24. Sketch map of Saransk and its environs (not to scale): Roman numerals, reference areas for sampling technogenic silts; CTP, city treatment plants.

material transported by sewage and surface runoff from developed areas are involved in sedimentation, poorly sorted sandy, fine-grained silty, and coarse-grained silts, represented by cohesive soils, are widespread in the Pakhra River, the grain size distribution of which is dominated by the silt fraction (35.1–53.8%); the share of clay particles is 1.5–7.4%; and silt and clay, 5.9–16.1%. The median size of the particles making up the silt varies within 0.031–0.075 mm. An important feature of the silt composition is a significant (by an order of magnitude) increase in the number of particles corresponding to silt–clay size, which largely determines the most important physical and adsorption–desorption properties of silts (plasticity, stickiness, cohesiveness, and moisture and chemical retention).

Mordovia region. Here, background alluvium (0–20 cm layer) was collected in the upper reaches of the Insar River, where there are no direct sources of technogenic pollution. Technogenic silts (their 20–60 cm layer was used for analysis) were collected within and below Saransk in the following areas (Fig. 24): Insar, area I, below the Lepeleyka River (taken as the zero mark; the distance from it is indicated below); II, center of Saransk (8 km); III, below Nikitinsky Creek (11 km); IV, above urban treatment plants (UTPs, 17 km); V, 0.2 km below UTPs (19.5 km), VI, 24 km (Fig. 24); X, 62 km; and also area XII of the Alatyr River, marginal part of the technogenic sedimentation zone (~70 km below the mouth of the Insar).

Technogenic silts that form in the channels of the Insar and Alatyr rivers are characterized by a peculiar grain size distribution (Table 26). Whereas sand fractions predominate in the background alluvium (especially the 0.5–0.25 mm fraction), the share of silt and clay particles is small (5.3 and 1.8%, respectively); the amount of silt and clay averages 3.5%; the silt fraction reaches 30–50%; the clay fraction, 10–25%; silt–clay, 11–32%. As already noted, particles less than 0.15 mm in size dominate in SS (up to 65–90%); i.e., technogenic SPM also contains significant amounts of silt particles. This clearly determines their increased content in silts.

The differences in the alluvium and silt composition are illustrated particularly well by the values of different indicators (Tables 27, 28). In particular, the median diameter (Q_{50}) of silt particles are three to ten times smaller than alluvium, for which the values of this parameter are close to the average value (0.3 mm) for rivers of a given geographic area. Silts have a high dispersion coefficient K_d (the ratio of the silt–clay

Table 26. Grain size distribution of background alluvium (BA) and technogenic silts (I–VIII), %

Sampling sites	Fractions, mm									
	2–1	1–0.5	0.5–0.25	0.25–0.10	0.10–0.05	0.05–0.01	0.01–0.005	0.005–0.001	<0.001	<0.01 (silt–clay)
	sand					silt		clay		
BA	1.2	19.2	51.6	16.2	5.8	2.5	1.7	1.1	0.7	3.5
I	0.1	2.0	15.5	12.0	17.1	25.6	3.2	14.14	10.1	27.4
II	0.1	1.6	9.0	6.7	13.1	37.3	10.3	16.0	6.0	32.3
III	1.0	8.5	30.3	10.5	14.7	19.4	3.7	9.0	2.9	15.6
IV	0.2	1.1	5.7	21.8	32.8	12.6	2.6	16.7	6.5	25.8
V	0.1	2.2	23.0	17.6	14.7	17.7	6.4	11.9	6.4	24.7
VI	0.1	0.4	4.1	6.4	17.0	42.0	9.7	14.6	5.7	30.0
X	0.3	0.7	5.4	13.4	38.8	24.2	5.5	9.5	5.2	20.2
XII	0.1	0.1	4.2	47.9	32.8	3.7	1.7	3.9	5.6	11.2

Table 27. Grain size characteristics of background alluvium (BA) and silts (I–VI, X, XII)

Area	Median diameter, Q_{50}	Sorting coefficient, So	Dispersity, Kd	Q_{90}/Q_{10}	Particle size class	
					after M.V. Klenovaya*	after N.M. Strakhov**
BA	0.220	2	0.04	8.5	Sand	Sand
I	0.020	35	0.38	470	Sandy silt	Fine-grained silt
II	0.015	11	0.48	313	Silt	Fine-grained silt
III	0.075	17	0.19	88	Sandy silt	Coarse-grained silt
IV	0.049	17	0.35	207	Sandy silt	Fine-grained silt
V	0.053	20	0.33	333	Sandy silt	Coarse-grained silt
VI	0.015	4	0.43	106	Silt	Fine-grained silt
X	0.035	8	0.25	90	Sandy silt	Fine-grained silt
XII	0.078	3	0.11	41	Sandy silt	Coarse-grained silt

* Based on relative silt–clay content (<0.01 mm fraction); ** based on average (median) diameter (Q_{50}).

content to the amount of other fractions), which is an order of magnitude greater than that of background alluvium. Whereas the alluvium is characterized by relatively good or intermediate sorting, the silts are poorly sorted, which is also confirmed by very high quantile ratios Q_{90}/Q_{10}. Based on the value of this indicator, background alluvium can be attributed to sediments homogeneous in particle size.

In most cases, technogenic silts are so-called cohesive plastic soils (Q_{50} very rarely exceeds 0.05 mm, and if it does, it does so insignificantly), whereas background alluvium is typical loose soil (Q_{50} much greater than 0.05 mm). It should also be mentioned that the asymmetry coefficient S_c of background alluvium is greater than unity, while technogenic silts are always less than unity. It is significant that the grain size coefficients calculated for the Insar's background alluvium are close to those typical of alluvial sediments in the rivers of central areas of the Russian Plain. Thus, the median diameter for alluvium of point bars here is 0.31–0.40; for the wide parts of rivers, 0.30–0.35; the sorting coefficient for bar formations is 1.23–1.28; for sediments in the wide parts of rivers, 1.26–1.32 (Lazarenko, 1964).

Table 28. Grain size characteristics of background alluvium (BA) and silts (I–VI, X, XII)

Area	Q_{10}	Q_{25}	Q_{75}	Q_{90}	S_k
BA	0.065	0.16	0.32	0.550	1.06
I	0.0005	0.0025	0.088	0.235	0.55
II	0.00075	0.004	0.045	0.235	0.40
III	0.0040	0.015	0.260	0.350	0.69
IV	0.0007	0.0047	0.080	0.145	0.16
V	0.00075	0.0075	0.150	0.250	0.40
VI	0.00075	0.005	0.030	0.080	0.66
X	0.001	0.0089	0.072	0.090	0.52
XII	0.005	0.043	0.130	0.205	0.92

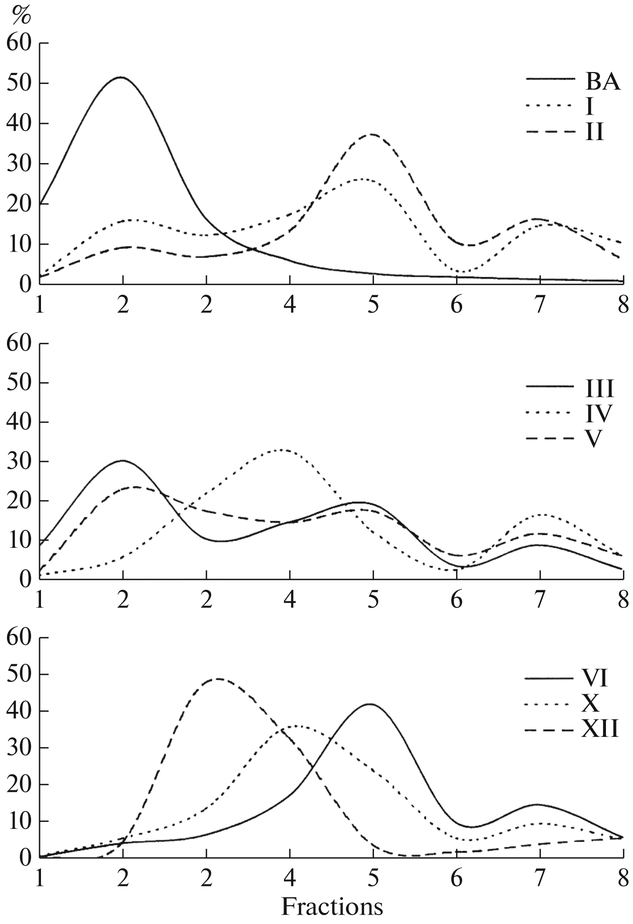

Fig. 25. Grain size distribution in background alluvium (BA) and technogenic silts (areas I–VI, X, XII): %, share of fraction; particle size, mm: 1, 2–1; 2, 1–0.5; 3, 0.5–0.25; 4, 0.25–0.10; 5, 0.10–0.05; 6, 0.05–0.01; 7, 0.01–0.005; 8, <0.005.

The Insar's background alluvium, which is dominated by medium-grained sand, is characterized by a single-peak particle distribution curve with pronounced asymmetry, which indicates the leading role of one source supplying sediment to the watercourse (soil and rocks of the catchment area). The curves for silts look completely different (Fig. 25). As is known, multipeak distribution curves are typical of sediments consisting of genetically inhomogeneous formations. In our case, this indicates that the silts consist of both natural and technogenic material. The similar appearance of the distribution curves for silts that form in areas of main technogenic material supply (Fig. 26, areas I, III, V) points to a certain uniformity in its grain size distribution and indicates the important role of hydraulic sedimentation of SPM in silt accumulation here. The three-peak character of the grain size distribution curves clearly reflects the sedimentary material transported by both city wastewater and surface runoff. In turn, for silts making up the riverbed within and below the city, the two-peak character of such curves corresponds to the significant participation of natural material in their formation. In addition, in these areas, SPM settles from the flow not only due to hydraulic sedimentation, but also due to coagulation of fine particles and colloids and the formation of amorphous matter due to sorption and flocculation processes, followed by their sedimentation. At the end of the technogenic sedimentation zone (area XII), the distribution curve becomes nearly single-peak, similar to that for background alluvium. Fine- and very-fine-grained sand dominates here, although the silt–clay content is also large.

With increasing distance from the city, there is also an increase in the degree of silt sorting and the median particle diameters, as well as a decrease in their dispersity. This is due to silt redeposition and their blending with natural sedimentary material, which is accompanied by an increase in sediment grain size; in their grain size parameters, the silts are close to background channel alluvium, which is quite clearly manifested in the spatial ratio of the sand, silt, and clay fractions (Fig. 27). The high silt–clay content in silts makes it possible, based on its spatial distribution, to reliably localize the city's zone of influence on the watercourse (Fig. 28).

Thus, the main features in the grain size distribution of technogenic silts widespread in the direction of the Insar manifest themselves as an increase in the silt–clay content. Silts differ particularly sharply from background alluvium by a significant increase in the relative particle size of the silt–clay fraction. In most cases, the background alluvium is medium-grained sand with gravel and pebble inclusions and a low clay content, characterized by good sorting. In the technogenic pollution zone, sandy or fine-grained silty (sometimes coarse-grained silty) sediments form in the channel. They are distinguished by poor sorting. From the engineering–geological aspect, alluvium is attributed to loose soils, and silts, to cohesive soils. Silts are highly erosion-resistant and affect channel processes and dynamics.

Kazakhstan region. The background areas of the Nura's channel are covered with typical channel alluvium, which are predominantly sand varieties mainly with a quartz composition. Grain size analysis of alluvium showed predominant coarse- (about 57%) and medium-grained (about 30%) sand. The proportion of silt and clay in the alluvium is insignificant (Tables 29, 30).

The share of clay particles (up to 10–20%), as well as fine- and very-fine-grained sand and silt, is appreciably elevated in technogenic silts. No directional trend in the vertical distribution of various fractions has been recorded in silts. Their inhomogeneous distribution is usually observed, resulting in alternating layers of silts enriched in either fine- or coarser-grained fractions (Fig. 29). This inhomogeneity is most pronounced for the sand (main natural component) and silt (technogenic component) fractions. Downstream, first, a general decrease in the content of finer fractions, especially silt, is observed, followed by enrichment of the lower silt layer in sand particles and depletion in clay and silt particles. This indicates differentiation of sedimentary material and its redeposition, involving fine sediment fractions in channel transport.

Thus, background alluvium is predominantly mixed sand with gravel and pebble inclusions and low silt and clay contents. The share of the sand fractions reaches 80–95%; clay, 0.6–3%. The morphometric characteristics and indicators of alluvium are close to the zonal values inherent to a given natural region. Alluvium is characterized by good sorting. In the technogenic pollution zone, sediments form in riverbeds consisting of sandy or fine-grained (sometimes coarse-grain) silts characterized by poor sorting. The share of sand fractions in technogenic silt decreases to 40–60%; the silt fraction increases to 25–50%; and clay, to 8–26%. Their main morphometric characteristics and indicators differ from background alluvium. Whereas the average (median) size of alluvium particles is 0.1–0.2 mm, the average (median) size of particles making up silts ranges from 0.015 to 0.078 mm. A characteristic feature of the silt composition is a sharp increase in the number of particles corresponding to of silt–clay fraction (<0.01 mm). Whereas in alluvium its share usually does not exceed 1–3.5%, in silt it reaches 10–32%, which determines the most important physical properties of the silts (plasticity, stickiness, cohesion, adsorption–desorption properties, and moisture and chemical retention). From the engineering–geological viewpoint, background alluvium pertains to loose soils, and silts, to cohesive soils, which are predominantly poorly sorted sandy, fine-grained, and coarse-grained silts. The silts, which are distinguished by a high amount of silt–clay particles and organic matter, are highly erosion-resistant, form various types of channel relief, and affect channel processes and dynamics.

Mineral Composition of Technogenic Silts

The mineralogical features of natural alluvium of lowland (primarily large and medium-sized) rivers are relatively well established; mineral assemblages typical of channel sediments have been identified, the qualitative composition of which is relatively stable and largely corresponds to the mineralogical complexes of the source rocks (Lazarenko, 1964; Lunev, 1967; Osovetsky, 2003; Allen, 1965). The mineral composition of technogenic silts has not been fully studied. The material below, obtained in the Pakhra and Nura river basins, partly fills this gap.

Moscow region. In the Pakhra basin, samples of channel sediments (0–20 cm layer) were collected within the background area (typical alluvium represented by medium-grained sands with gravel and peb-

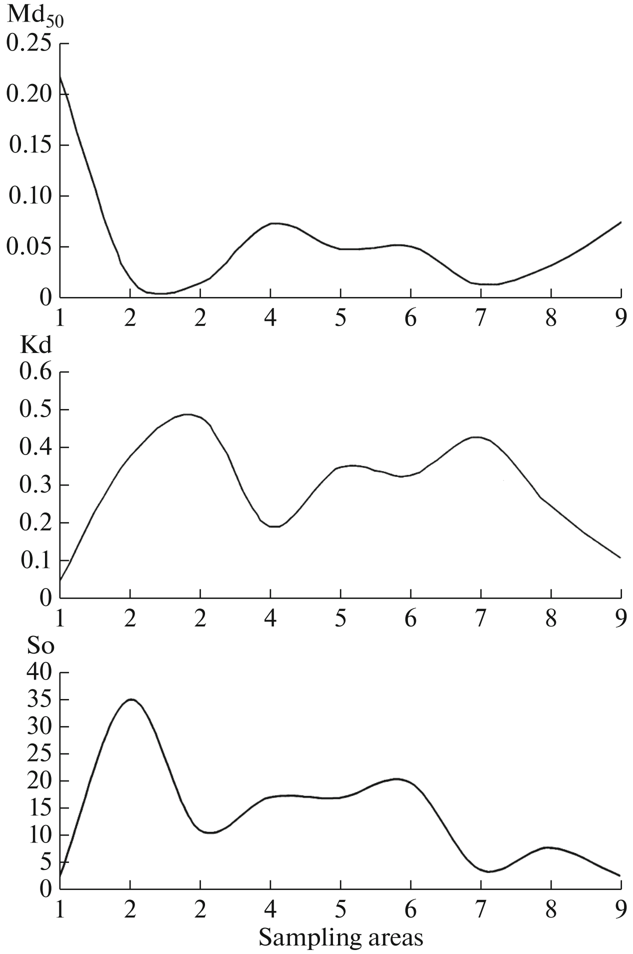

Fig. 26. Grain size distribution in background alluvium (BA) and technogenic silts. Areas: 1, background; 2–7, I–VI; 8, X; 9, XII; Md, median diameter; Kd is dispersion coefficient; So, sorting coefficient.

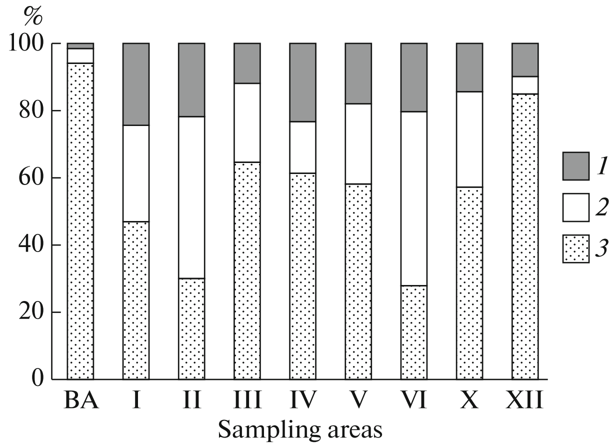

Fig. 27. Particle structure of background alluvium (BA) and technogenic silts (areas I–VI, X, XII): (*1*) clay, (*2*) silt (*3*) sand.

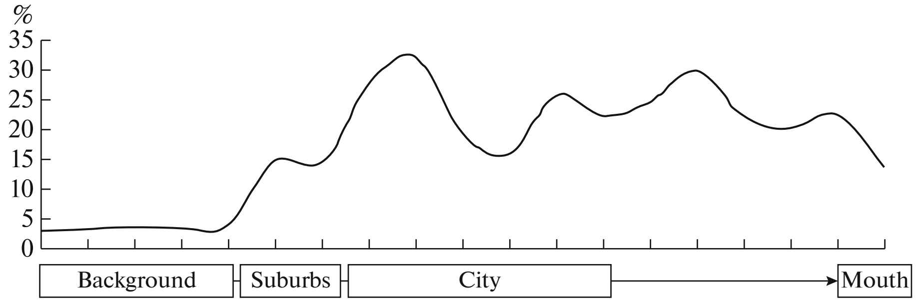

Fig. 28. Distribution of silt–clay in channel deposits of Insar River in zone of influence of Saransk.

ble inclusions); in agricultural watercourses (light-silty, medium-grained sands), in the Pakhra River, in the zone of influence of Podolsk (technogenic silts), and in reservoirs and streams draining the Shcherbinsky landfill (technogenic silts) (Yanin, 2004a, 2007a). Samples of sediments in their natural form, without removal of carbonates and amorphous matter, were separated by bromoform (specific gravity 2.9 g/cm^3) for the light and heavy fractions, each of which was examined under a polarizing microscope in immersion fluids. The content of individual minerals in the corresponding fraction was calculated as the percentage of the total number of grains counted in each preparation. Differential thermal analysis of samples was carried out on an MOM derivatograph. Part of the selected channel samples, as well as samples of SS generated at treatment plants in Podolsk and Klimovsk, were investigated by X-ray phase semiquantitative analysis. To characterize the sediments, the indicators and coefficients used in mineralogy were calculated (Berger, 1986; Dobrovolsky, 1966; Kazansky, 1969; Osovetsky, 2003). The grouping of minerals

Table 29. Grain size distribution of technogenic silts and background alluvium, Nura River, %

Silt horizon, cm	Fraction, mm						
	sand					silt	clay
	coarse	large	medium	small	fine		
	2–1	1–0.5	0.5–0.25	0.25–0.1	0.1–0.063	0.063–0.004	<0.004
3 km below main sewage canal							
0–20	2.7	3.1	54.5	7.8	16.1	3.8	12.0
20–40	2.6	3.1	3.7	5.2	12.7	50.8	21.9
40–60	2.5	3.0	56.7	7.9	15.9	3.9	10.0
60–80	0.7	0.7	17.0	19.0	21.0	15.0	26.6
80–100	2.0	3.0	13.0	39.0	1.0	22.0	20.0
100–120	0.7	0.7	28.7	3.3	50.0	3.3	13.3
120–140	5.7	3.0	3.5	13.2	6.8	49.9	17.9
9 km below main wastewater canal							
40–60	1.3	3.4	27.2	31.5	8.4	5.3	22.9
80–100	0.3	8.0	27.0	31.4	12.1	5.1	16.1
120–140	0.6	22.0	24.8	32.6	12.1	1.4	6.5
32 km below main wastewater canal							
20–40	0.6	9.3	31.6	32.7	8.2	5.4	12.2
105 km below main wastewater canal							
20–40	0.1	2.2	31.0	30.1	8.8	5.2	22.6
90–120	0.3	27.4	36.9	25.9	2.1	0.8	6.7
Background alluvium (headwaters of Nura River)							
0–30	6.6	57.4	30.2	1.9	0.5	0.3	3.1

according to their stability and migration ability in the hypergenesis zone was based on information in the literature (Berger, 1986; Dobrovolsky, 1966; Yakhontova and Zvereva, 2000) (Tables 31, 32).

In the light fraction of the Pakhra's alluvium, quartz dominates (72%); feldspar (13.6%), modified minerals, and rock fragments (6.4%), and acid plagioclases (>4%) are present; in the heavy fraction, hornblende (24%), black ore minerals (>22%), epidote (>18%), garnet (>7%), zircon (>6%) prevail (Table 33).

On the whole, the mineral composition of the Pakhra's background alluvium is close to the composition of channel sediments in central areas of the Russian Plain. Thus, quartz (85–95%) predominates in the light fraction of channel sediments of the Dnieper, Desna and Oka rivers; feldspar (5–10%) and rock fragments (up to 2%) are prevalent; glauconite, carbonates, and weathered grains are present; the heavy alluvium fraction is dominated by the ilmenite–garnet–hornblende–epidote assemblage; staurolite, sillimanite, kyanite, zircon, rutile, tourmaline, and leucoxene are also found (Lazarenko, 1964). In the light fraction of alluvium of the upper reaches of the Dnieper, quartz (92–95%) and feldspar (5–8%) predominate; the ilmenite–almandine garnet–tourmaline assemblage dominates the heavy fraction.

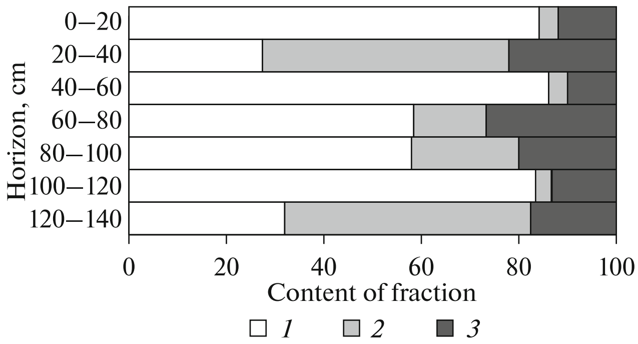

Fig. 29. Grain size distribution of technogenic silts of Nura River 3 km below MWC: (*1*) sand; (*2*) silt; (*3*) clay.

Thus, the relative constancy of the mineral composition of channel alluvium in these rivers reflects the similarity of mineral assemblages characteristic of the rock sources of sedimentary material for watercourses in this region; i.e., the main role in the formation of mineral assemblages peculiar to alluvium is played by supply areas (source and terrigenous-mineral prov-

Table 30. Grain size characteristics of background alluvium and technogenic silts, Nura River*

Layer, cm	Grain size coefficients and characteristics							Particle size class	
	average grain size, mm	Q_{50}	Q_{25}	Q_{75}	S_0	S_K	K_{cl}	after M.V. Klenovaya**	after N.M. Strakhov***
Background alluvium, headwaters									
0–30	0.66	0.425	0.288	0.624	2.2	0.99	0.03	Sand	Sand
3 km below main wastewater canal									
0–20	0.29	0.210	0.052	0.288	5.5	0.36	0.14	Sandy silt	Sand
20–40	0.11	0.008	0.003	0.020	7.7	0.90	0.28	Clay silt	Clay silt
40–60	0.29	0.200	0.060	0.287	4.8	0.41	0.11	Sandy silt	Sand
60–80	0.17	0.040	0.002	0.100	66.7	0.09	0.36	Silt	Fine-grained silt
80–100	0.17	0.088	0.004	0.145	39.8	0.07	0.25	Silt	Coarse-grained silt
100–120	0.17	0.053	0.023	0.190	8.3	1.60	0.15	Sandy silt	Coarse-grained silt
120–140	0.17	0.007	0.003	0.075	24.2	4.10	0.22	Clay Silt	Clay silt
9 km below main wastewater canal									
40–60	0.20	0.095	0.004	0.205	51.3	0.09	0.30	Sandy silt	Coarse-grained silt
80–100	0.23	0.097	0.034	0.221	6.5	0.79	0.19	Sandy silt	Coarse-grained silt
120–140	0.37	0.145	0.085	0.350	4.1	1.40	0.07	Silty sand	Sand
32 km below main wastewater canal									
20–40	0.25	0.145	0.072	0.250	3.4	0.86	0.14	Sandy silt	Sand
105 km below main wastewater canal									
20–40	0.19	0.093	0.005	0.218	41.9	0.13	0.29	Sandy silt	Coarse-grained silt
90–120	0.39	0.235	0.100	0.405	4.1	0.73	0.07	Silty sand	Sand

* Calculated according to the Table 29; ** according to relative clay-and-silt content (<0.01 mm fractions); *** based on average (median) diameter (Q_{50}).

Table 31. Grouping of minerals according to their behavior in hypergenesis zone

Estimate	Chemical stability	Physical and mechanical stability	Hydrodynamic stability	Migration ability
High	Anatase, kyanite, leucoxene, rutile, staurolite, tourmaline, zircon, quartz	Garnet, staurolite, tourmaline, zircon, quartz	Rutile, zircon	Anatase, garnet, kyanite, leucoxene, rutile, staurolite, tourmaline, zircon, quartz, microcline
Average	Apatite, garnet, titanite, microcline	Anatase, apatite, kyanite, leucoxene, pyroxenes, hornblende, rutile, titanite, tremolite–actinolite, epidote, microcline, plagioclase, feldspar	Anatase, garnet, kyanite, leucoxene, staurolite, titanite	Hornblende, titanite, epidote, plagioclase
Low	Pyroxenes, plagioclases, feldspars, hornblende, tremolite–actinolite, epidote, glauconite	Glauconite	Apatite, pyroxenes, hornblende, tremolite–actinolite, tourmaline, epidote, glauconite, quartz, microcline, feldspar	Apatite, pyroxenes, tremolite–actinolite, glauconite, feldspar

Table 32. Scales of hydrodynamic, chemical, and physicochemical maturity of terrigenous minerals (TM)

Maturity estimate	Hydroaerodynamic maturity of the heavy fraction (with exception of authigenic), %	Chemical maturity of heavy fraction (total HM content with high and very high chemical stability)	Chemical and physicochemical maturity	
			J. Hubert's ZTR index (total content of most stable TM: zircon, rutile, tourmaline)	quartz, light fraction, %
Very low	<1	<20	<60	<60
Low	1–2	20–40	60–70	60–70
Average	2–5	40–60	70–80	70–80
High	5–10	60–80	80–90	80–90
Very high	10–20	81–95	90–95	90–95
Exceptionally high	>20	>95	–	>095

inces) and the petrographic composition of source rocks. The influence of other factors (neotectonics, migratory capacity of minerals, grain size composition of sediments) occurs against the background of qualitative and quantitative sets of minerals determined by the parent (source) rocks.

In areas of technogenic pollution, the mineral composition of Pakhra channel sediments undergoes appreciable changes, primarily manifested in disruption of the quantitative ratios of minerals associated with one another in natural background alluvium conditions. In addition, technogenic contain minerals not found in watercourse sediments of background and agricultural areas, but which are typical of industrial impact conditions (portlandite, pyrite–marcasite, etc.). The degree of change in the mineral composition of sediments (in the studied series background–agricultural district–city–landfill) increases substantially. This indicates that the established changes are not due to possible areal differences in the composition of parent rocks, but are primarily determined by the supply of technogenic sedimentary material into watercourses and their intensive chemical pollution. Thus, in the light fraction of channel sediments (in the studied series background–agricultural district–city–landfill) the following are observed (Tables 33, 34; Figs. 30, 31): (1) a directional reduction in quartz and feldspar content, as well as altered minerals, rock fragments, and microcline; (2) a significant increase in the amount of carbonate minerals, especially in the zone of influence of the city; (3) an increase in the content of acidic (Na–Ca) plagioclase and glauconite in silts (especially in the zone of influence of the city); (5) accumulation of significant amounts of limonitized fragments (especially in the zone of influence of the landfill) and portlandite in silts; (6) the occur-

Table 33. Average mineral composition of channel sediments of Pakhra River basin

Minerals	District			
	background	agricultural district	city	landfill
Light fraction (total = 100%)				
Quartz	71.87	69.44	60.45	63.01
Feldspar	13.60	13.56	11.48	8.26
Acid plagioclase	4.13	4.00	6.14	5.32
Microcline	2.28	1.53	1.24	1.32
Glauconite	0.57	0.78	1.97	1.0
Carbonate minerals	0.32	3.39	12.22	5.53
Portlandite	–	–	1	0.5
Altered minerals and clasts	6.40	5.15	2.59	2.05
Limonitized clasts	–	–	2.10	13.0
Other	0.83	2.15	0.81	0.10
Heavy fraction (total = 100%)				
Black ore minerals	22.68	20.13	24.81	20.00
Common hornblende	24.05	23.75	14.04	8.83
Iron hydroxides	3.97	5.78	10.84	26.43
Altered minerals and clasts	1.82	1.83	0.72	1.83
Leucoxene	1.57	1.05	1.22	1.03
Garnet	7.23	8.57	7.28	8.80
Monoclinic pyroxenes	0.83	1.83	1.06	0.27
Orthopyroxenes	0.50	0.52	0.22	–
Tremolite–actinolite	2.20	2.11	1.25	0.97
Epidote	18.38	15.87	12.82	9.53
Zircon	6.65	5.32	8.41	6.50
Staurolite	0.97	1.32	1.46	1.83
Tourmaline	0.88	1.05	1.83	1.88
Kyanite	1.51	1.43	4.33	4.10
Rutile	1.93	1.36	2.67	2.03
Anatase	0.82	0.68	1.17	1.03
Titanite	0.93	0.76	0.59	0.52
Apatite	1.53	3.53	1.28	1.17
Other	1.55	3.11	4.00	3.25
Yield of heavy fraction, %	2.56	2.93	3.64	3.49
Number of samples	7	10	10	7

There are 286–376 total grains in the light fraction, and in the heavy fraction, 305–471. Among other minerals, individual samples in the light fraction contain ubiquitous single grains of biotite, medium basic plagioclase; in the zone of the city and landfill, chlorite, muscovite, chalcedony fragments, volcanic basic glass; in the landfill zone, volcanic acid glass; the heavy fraction in the zone of the city and landfill contains single grains of pyrite–marcasite, spinel, andalusite, corundum, chloritoids, Cr-spinel, aegirine, olivine, siderite, sillimanite, barite–celestine. The total heavy fraction in the alluvium of lowland rivers is usually 1–0.1%.

rence of chlorite, muscovite, chalcedony fragments, and volcanic basic and acid glass in silts in the zones of influence of the city and landfill.

Thus, in areas of technogenic pollution, the main rock-forming minerals (quartz and feldspar) are “displaced” by various new formations (carbonate minerals, limonitized debris), and, to a certain extent, authigenic minerals (glauconite). The presence of portlandite, a typical mineral in cement and coal ash, is a characteristic indicator of technogenic impact.

The percentage of quartz is usually considered an indicator of the chemical maturity of the terrigenous mineral assemblage in the light fraction (Berger, 1986). From these positions, background channel

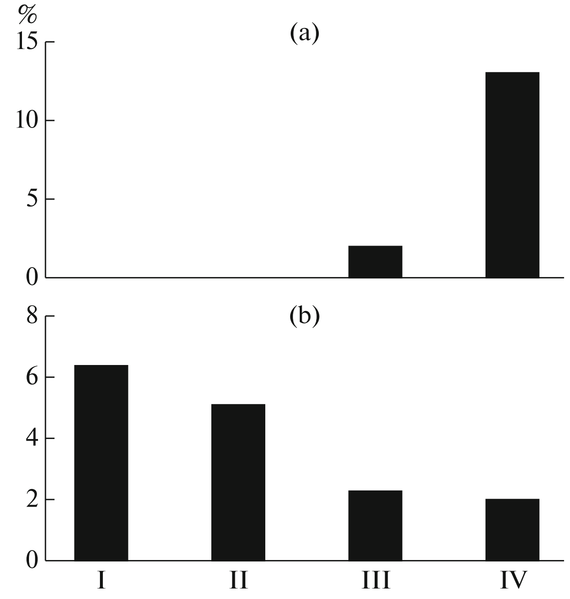

Fig. 30. Limonitized fragments (a) and altered minerals and clasts (b) in channel deposits of Pakhra River basin. Here and in Figs. 31–33: I, background area; II, agricultural district; III, city; IV, landfill.

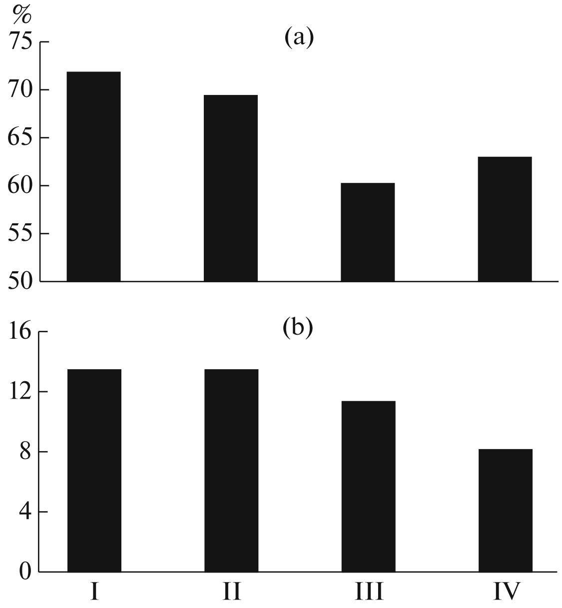

Fig. 31. Quartz (a) and feldspars (b) in channel deposits, Pakhra River basin.

alluvium (more "worn out," as referred to in the old geological literature, hypergenic processes) is characterized by moderate chemical maturity, and technogenic silts, like young sedimentary formations, are characterized by low chemical maturity.

In areas of technogenic impact, significant changes are also observed in the composition of the heavy sediment fraction, with a simultaneous increase in its yield. According to (Berger, 1986; Lazarenko, 1964), even a slight increase in the heavy fraction in natural alluvium is accompanied by transformation of its composition: an increase in the relative amount of the heaviest terrigenous minerals (zircon, rutile) compared to the content of lighter minerals in this fraction (tourmaline, sillimanite, andalusite). In our case, this hardly occurs: in the pollution zone, technogenic silts demonstrate a slight increase in rutile content, irregular variation in the amount of zircon, and even a slight increase in tourmaline content. The changes in the composition of the heavy fraction of channel sediments in the Pakhra basin are especially evident in the values of various mineralogical indicators and ratios (Tables 35, 36). Whereas in the heavy fraction of background alluvium, the total share of black ore minerals, hornblende, and epidote (the main minerals of the background assemblage) is more than 65%, in channel sediments of agriculture district rivers, it is less than 60%; below the city, about 52%; in the landfill's zone of influence, only 38%.

Whereas for black ore minerals as a whole, their content varies slightly in the studied sediments (only a slight increase in their number in the zone of influence of the city can be observed, which, e.g., may be due to the formation of brown iron ore as a result of oxidation of iron-containing hydrogenous minerals) in the series background–agricultural district–city–landfill, there is a directional decrease in the hornblende and epidote contents typical of mineral alluvium in the central regions of Russia (Fig. 32).

Obviously, these minerals are contained in smaller quantities in technogenic sedimentary material enter-

Table 34. Mineralogical indicators of channel sediments of Pakhra River (light fraction)

District	Total feldspar, %	Quartz/other light-fraction minerals	Quartz/carbonate minerals	Feldspar/altered minerals and rock fragments	Glauconite + carbonate minerals/quartz
Background	20.01	2.55	225	3.34	0.01
Agricultural district	19.09	2.27	21	3.71	0.06
Urban	18.86	1.53	5	7.28	0.24
Landfill	14.90	1.70	11	7.27	0.10

Table 35. Mineralogical indicators of channel sediments of Pakhra River (heavy fraction)

District	Amount of stable minerals, %	J. Hubert ZTR Index	Fe hydroxides/ hornblende + garnet + epidote	Staurolite/kyanite	Local rock influence coefficient	Stability coefficient (stable minerals/ hornblende)	Hornblende/ Kyanite + staurolite	Fe hydroxides/ black ore minerals	Black Ore/ Hornblende	Hornblende/epidote (source rock ratio)
Background	14.33	9.45	0.08	0.64	12.6	0.6	9.7	0.18	0.94	1.1
Agricultural district	12.21	7.73	0.12	0.92	11.8	0.5	8.6	0.29	0.85	1.50
Urban	21.09	12.91	0.38	0.33	3.7	1.5	35.4	0.44	1.77	1.10
Landfill	18.04	10.41	0.97	0.45	3.0	2.0	1.5	1.32	2.27	0.93

Table 36. Ratio of minerals of various hydrodynamic stability and migration capacity in the heavy fraction of the channel sediments of Pakhra River

District	Minerals with high hydrodynamic stability, % (I)	Minerals with low hydrodynamic stability, % (II)	Ratio (I) : (II)	Minerals with high migration capacity, % (III)	Minerals with low migration capacity, % (IV)	Ratio (III) : (IV)
Background	8.58	48.37	0.18	21.56	5.06	4.3
Agricultural district	6.68	48.68	0.14	20.78	7.99	2.6
Urban	11.08	32.50	0.34	28.37	3.81	7.5
Landfill	8.53	22.65	0.38	27.20	2.41	11.3

ing the river, and, moreover, they are actively broken down in dynamic technogenic sedimentation conditions. In particular, hornblende and epidote, as well as titanite and pyroxene, are characterized by low chemical and physicochemical stability in the hypergenesis zone (Berger, 1986; Kazan, 1969).

In technogenic silts, there is an increase (compared to background alluvium) in the content of minerals that are stable in the hypergenesis zone, such as staurolite, kyanite, rutile, anatase, and tourmaline. Pyrite–marcasite, corundum, and certain other minerals absent in alluvium are also found in silts (single grains). The increased content of agricultural district apatite in river sediments is clearly due to the use of mineral fertilizers here. Lower staurolite/kyanite ratios in the zones of influence of the city and landfill suggest that, compared to alluvium, technogenic silts are at an active postsedimentary transformation stage. In the general case, an increase in the content of accessory minerals stable in the hypergenesis zone is observed in technogenic channel sediments (from 14% in background alluvium to 18–21% in technogenic silts), which is reflected as an increase in the stability coefficients (from 0.6 to 1.5–2); an appreciable decrease in the share of minerals with low hydrodynamic stability (from 48 to 22–32%) and low migration ability (from 5 to 3–4%) has also been recorded. It is interesting to note that in the series background–agricultural district–city–landfill, there is a directional increase in the total amount of minerals with pronounced magnetic susceptibility. This is obviously characteristic of bottom sediments of technogenic pollution zones. Thus, the sediments of Tees River (UK), which has industrial and mining facilities in its catchment area, also has been found to contain elevated levels of magnetic minerals (Plater et al., 1999). The latter, in the opinion of the authors of the cited work, are indicators of river pollution by technogenic substances.

A striking feature of technogenic silts is the increased amount of new formations in them, primarily carbonate minerals, iron hydroxides (Fig. 33), and limonitized fragments (Table 34). The increase in carbonate mineral content in sediments of agricultural district watercourses is apparently due to the long-term use of mineral fertilizers here. In the zone of influence of the city, carbonate minerals in significant quantities are transported as part of wastewater SPM. It is also known (Lazarenko, 1964) that carbonates are characterized by the finest fractions of river sediments, indicating their formation due to SPM sedimentation. This may partly explain the high amount of carbonate minerals in silts in the zone of influence of the city. In reservoirs and streams draining the landfill, a chemogenic pathway for the formation of carbonate minerals cannot be excluded.

In the heavy fraction of channel sediments, the most common new formations are iron hydroxides, and their amount in technogenic silts, especially those

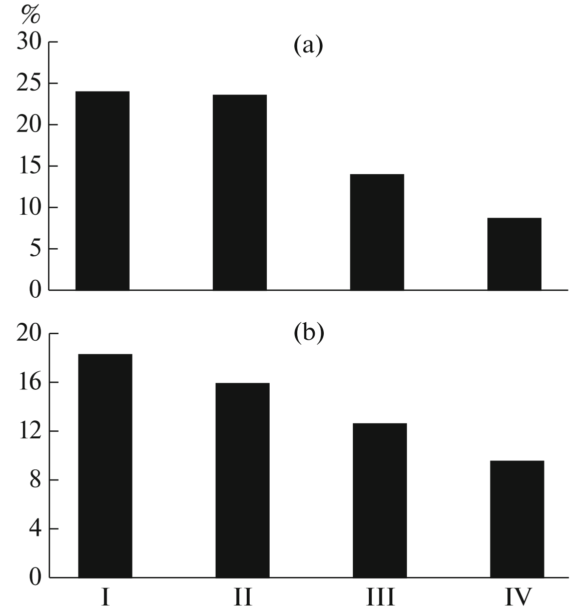

Fig. 32. Ordinary hornblende (a) and epidote (b) in channel deposits, Pakhra River basin.

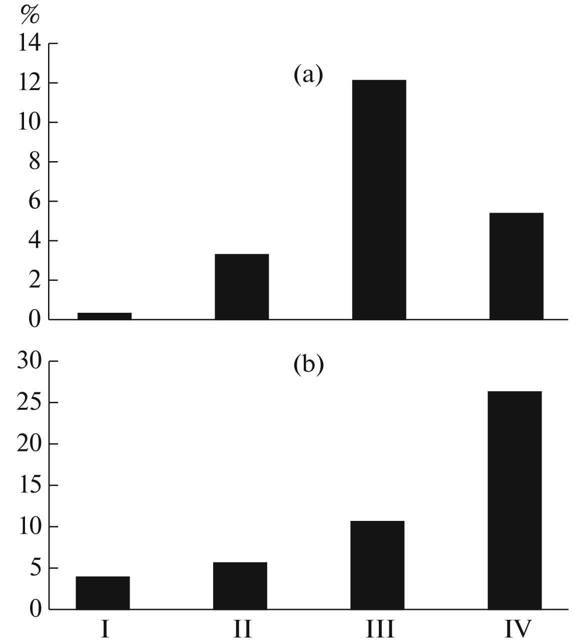

Fig. 33. Carbonate minerals (a) and iron hydroxides (b) in channel deposits, Pakhra River basin.

formed in reservoirs and landfill streams, increases significantly. It is well known that under technogenic pollution conditions, the supply of iron into rivers in the composition of wastewater is always large. As it migrates in the channel, iron is oxidized, which is partly due to the weakly alkaline medium of the main mass of river waters, and partly to subsequent sedimentation as a mixture of oxides and hydroxides. As a result of hydration, iron oxides absorb water and become hydrated iron oxides or hydroxides (Olier, 1987). Over time (natural aging), transition of amorphous iron hydroxides to crystalline varieties—goethite, hematite, limonite—is possible (Gorbunov, 1963). Organic acids in silt waters and low oxygen concentration contribute to this (Yakhontova and Zvereva, 2000). In streams and reservoirs of the landfill, where the maximum iron hydroxide content is observed, the alkaline medium contributes to their sedimentation. The high content of iron hydroxides causes an increased iron content in technogenic silts.

The presence of significant amounts of limonitized debris in technogenic silts is apparently a phenomenon typical of such sediments. Limonite can accumulate due to the breakdown of iron humate compounds under the action of oxygen (in river water, a substantial share of dissolved iron is associated with humic colloids). It is believed that limonization is takes place at almost all stages in the formation of the hypergenesis zone; only minerals that are mechanical impurities in limonite are altered (Yakhontova and Zvereva, 2000).

In technogenic silts of the Pakhra River and its tributaries, amorphous alumina (0.3–13.9%) and calcite (0.7–10.7%) are observed almost everywhere, and dolomite, gypsum, anhydrite, amorphous carbonate, pyrite, marcasite, jarosite, and diaspore are quite frequently encountered. It is known that under the natural conditions of the central Russian Plain, these new mineral formations, as a rule, are characteristic of old, floodplain, boggy, and much less frequently, channel silt sediments (Lazarenko, 1964). Nevertheless, their presence in technogenic channel silts is natural, since these typical hypergene and authigenic minerals enter watercourses as a part of technogenic SPM and are formed directly in the river medium under specific technogenic sedimentation conditions even at the early diagenesis stage of alluvial sediments. In addition, significant amounts of amorphous alumina (2.5–5.6%), calcite (up to 1.7%), dolomite (up to 1.5%), and gypsum (up to 0.8%) have been found in Podolsk sewage sludge (SS). These minerals, typical of technogenic conditions, apparently form during treatment of wastewater and subsequent placement of SS in sludge drying beds; they can also flow directly into a watercourse.

The presence of pyrite and marcasite in silts (especially in landfill waters and in places of their highest accumulation) indicates a reducing environment in sediments. Whereas in natural alluvium, new sulfate formations are very rare, since sulfate mineralization is ephemeral, short-lived, and easily transformable (Lazarenko, 1964), the presence of gypsum in technogenic sediments indicates sulfate formation processes occurring in them, owing to significant amounts of calcium in silts and wastewater with a high sulfate content. The formation of mineral salts during sewage treatment at treatment plants and their entry into the river as a part of technogenic SPM cannot be excluded. The finding in Pakhra River sediments below the confluence with the Oranka River of such rare (for this river basin) minerals as rankinite and hydrosodalite are probably the result of Troitsk wastewater entering Oranka Creek. It should be noted that many authigenic minerals, mineral groups, and isomorphous series typical of technogenic silts can flow into watercourses with surface runoff from urban areas.

In terrigenous mineralogy, the so-called local rock influence coefficient is commonly used to assess the degree of influence of local, more ancient sedimentary rocks on the composition of Quaternary sediments. It is believed that low values of this coefficient indicate increased participation of detritus of more ancient rocks in the composition of Quaternary sediments (Dobrovolsky, 1966). For example, for alluvial sands of the Belarusian Dnieper, the values of the coefficients of local rock influence are 9.7–17.2 (Kuznetsov, 1973). Similar indicators for channel sediments of the background and agricultural areas of the Pakhra River basin are 12.6 and 11.8, respectively, and for technogenic silts, they decrease to 3–3.7. The appreciable decrease in this coefficient in the zones of influence of the city and landfill clearly indicates that widespread technogenic sedimentary material transported from developed territories plays the leading role in forming the mineral composition.

As noted above, technogenic silts have a significant amount of amorphous (X-ray amorphous) matter. Whereas in the background conditions of the Pakhra River basin, the share of the amorphous phase in channel alluvium is about 11%, in technogenic silts, it increases to 30% or more (Fig. 34, Table 37). A high share of amorphous matter in urban SS suggests that sewage (technogenic SPM) is their main source of input into watercourses.

The amorphous matter present in silts plays an important geochemical role, largely determining their significance, on the one hand, as pollutant concentrators, and on the other, as potential sources of secondary pollution of the water mass during sediment diagenesis. The presence of significant amounts of X-ray amorphous matter in sediments significantly increases their colloidal activity, swelling, water permeability, stickiness, and hydrophilicity (Gorbunov, 1963). Amorphous matter formed in the hypergenesis zone and entering sedimentation basins gives rise to various new formations, which often represent complex polymorphic formations that are difficult to identify (Polikarpochkin, 1976; Yakhontova and Zvereva, 2000).

Differential thermal analysis has shown the presence of clay minerals in technogenic silts, whereas in the background alluvium of the Pakhra River, they barely registered on the differential curve. Based on XRD data, the amount of clay minerals (identified by illite) in the background alluvium does not exceed 0.1%. In areas of technogenic pollution, their amount increases markedly, varying from 0.2 to 3.4% (illite is present; to a lesser extent, kaolinite and chlorite, but rarely smectite). The clay mineral content (kaolinite, chlorite, smectite, illite) is especially high in SS produced at Podolsk treatment facilities.

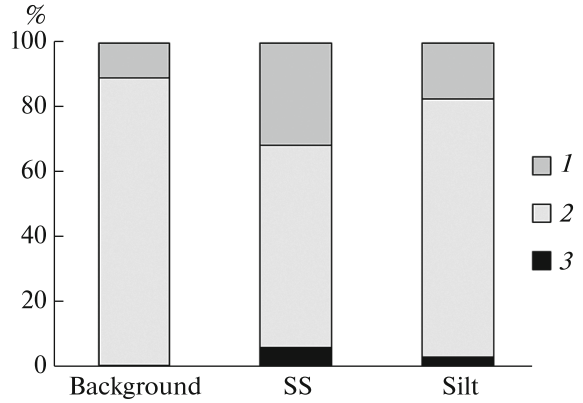

Fig. 34. Composition of background alluvium, SS of Podolsk, and technogenic silts of Pakhra River: (*1*) amorphous matter; (*2*) nonclay minerals; (*3*) clay minerals.

Thus, within an insignificant area of the Pakhra River basin, technogenic influence is manifested in the development of channel sediments significantly differing in their mineral composition. Under natural conditions, such sharp spatial changes in the mineral composition of channel alluvium within a single source province are rarely observed. As a rule, the observed spatial changes in the mineral composition of channel alluvium are insignificant and do fundamentally change the mineral association characteristic of the alluvium in this river.

Kazakhstan region. The main feature of the mineral composition of technogenic silts widespread in the Nura River is the low quartz content and very high amorphous matter content (Table 37) (Yanin, 2004b). In Nura technogenic silts, portlandite, a typical cement mineral, and hydrocaluminite, a very rare mineral associated with portlandite (formed from rare calcium silicates like larnite, found in limestone) have been identified. Both minerals are present in the waste products of the Karbid carbide production plant and in material in the hydro-ashdumps of the GRES-1 regional power station. It is known that in interaction with water, calcium oxide is an important component of ash; portlandite is formed in significant quantities; and due to the hydrolysis and hydration processes in ash landfills, hydrocalumite can also form. It is possible that they form directly in the river after technogenic sedimentation. The silt composition also contains thaumasite (a very rare mineral in nature, but present in significant amounts in carbide production waste) and calcite (which, as is well known, is the main mineral of limestone; it is also used in cement produc-

Table 37. Mineral composition of various technogenic formations in zone of influence of Temirtau, %

Sediments	Quartz	Albite	Potassium feldspar	Amphibole	Calcite	Calcium-aluminosilicate	Illite	Kaolinite
Slurry-1	2.9	–	–	–	18.4	–	tr.	tr.
Slurry-2	1	–	–	–	10.3	tr.	tr.	–
Slurry-3	1	–	–	–	8.2	tr.	tr.	–
SS-1	66.3	6.1	2.4	–	3.2	–	tr.	tr.
SS-2	7.5	0.5	tr.	–	tr.	–	tr.	–
SS-3	4.8	0.5	tr.	tr.	4.8	–	tr.	–
Ash	13.8	–	–	–	tr.	–	tr.	–
Epiphytic suspension	8.6	tr.	–	–	22.6	–	tr.	–
Technogenic silt	21.5	1.9	–	tr.	1.8	–	tr.	tr.

Sediments	Smectites	Mullite	Taumasite	Gypsum	Hematite	Portlandite	Hydrocalumite	DA
Slurry-1	tr.	–	24.6	–	–	tr.	2	~50
Slurry-2	tr.	–	tr.	tr.	–	24	3	~36
Slurry-3	tr.	–	tr.	tr.	–	29.5	3	~39
SS-1	tr.	–	–	–	–	–	–	~78
SS-2	tr.	–	–	7	0.5	–	–	~17
SS-3	tr.	tr.	–	–	0.5	–	–	~11
Ash	tr.	23	–	–	–	–	–	~37
Epiphytic suspension	tr.	–	–	–	–	–	–	~32
Technogenic silt	tr.	13.6	0.5	–	tr.	tr.	tr.	~40

Slurries: (1–3) carbide production waste: 1, from Zhaur swamp (old septic tank); 2, from existing landfill; 3, from old landfill; SS (1–3): 1, from mixing fields (runoff of chemical plant and household runoff in Temirtau); 2, old silt lagoons; 3, new silt lagoons; ash, material from ash landfills; epiphytic suspension (river suspension precipitated on macrophytes)—sample taken from Nura River below main wastewater canal; technogenic silts—Nura River, same area; DA, degree of amorphism (remainder, which is amorphous mass), %; tr., trace amounts.

tion and as flux in metallurgy). The presence of such clay minerals as smectites, illite, and kaolinite is typical.

The data given in Table 37 indicate that the main matrix of technogenic silts is to a significant extent material from the GRES-1 hydro-ashdumps, which entered the Nura River with slurries and emergency discharges; a lesser role is played by carbide waste and wastewater SPM. Thus, silts are distinguished by a high mullite content, usually an artificial product formed at high temperatures. It is well known that precisely coal ash is characterized by the presence of significant mullite-type sediments (containing over 70% alumina, which is reflected in the silt chemical composition) and high concentrations of amorphous clayey matter. It was also established that a high degree of amorphization of the structure, the predominant content of glassy particles of fine fractions, and the presence of calcium silicates and aluminates and free silica and alumina oxides facilitate coal ash activity, i.e., its ability to interact with calcium hydroxide to form hydrosilicates and hydroaluminates when mixed with water and other compounds, producing the structural formation of artificial stone. Accumulations (a massif) of such artificial stone (artificial sedimentite) were observed at the mouth of the main wastewater canal, where due to a decrease in water level in the Nura River, the upper part of the technogenic silt that accumulated passed into a semisubmerged state.

For channel sediments widespread in the rivers of urbanized areas, the presence of asbestos fibers is typical, which can play a role in forming the physical properties and chemical composition of technogenic silts (Yanin, 2008a). The presence of talc in river sediments cannot be excluded. In particular, talc has been used as a filler in powdered pesticides, which at one time were massively applied over large areas in many countries. In summer, the talc contained in pesticides was picked up by the wind and transported long distances. In addition, various technogenic particles that enter rivers with surface runoff and wastewater are almost always present in technogenic silts (Yanin, 2018). For example, numerous particles of slag, concrete, brick, artificial bitumen, fibrous materials, plastics, polyethylene, pieces of rubber, wood materials, small metal fragments, artificial glass fragments, etc., were constantly encountered in the Pakhra, Insar, and Nura river basins.

Table 38. Chemical composition of various sediments, %

Component	Q	BS	BA	SS	WS	Technogenic silts, Insar River, sampling area VI					
		sampling layer, cm									
		0–10	0–30	30–80	–	0–20	20–60	60–120	120–180	180–240	240–300
SiO_2	73.58	73.69	81.63	23.87	28.3	44.50	62.32	58.42	57.64	59.24	64.35
TiO_2	0.34	0.54	0.33	0.25	0.40	0.58	0.64	0.64	0.60	0.61	0.59
Al_2O_3	6.55	6.41	5.22	4.70	5.50	10.05	10.52	10.98	11.00	10.64	9.92
Fe_2O_3	2.10	2.59	4.03	1.04	4.16	3.22	4.24	3.73	3.93	4.72	5.17
FeO	0.94	0.47	0.57	3.00	3.20	2.65	1.36	2.66	3.74	2.30	1.41
MnO	0.044	0.20	0.078	0.04	–	0.048	0.075	0.079	0.076	0.070	0.057
CaO	5.23	0.47	0.78	8.00	8.14	4.10	2.20	2.20	1.80	1.72	1.72
MgO	1.94	0.70	0.37	1.40	2.32	0.92	1.16	1.36	1.05	1.05	0.84
Na_2O	0.30	0.55	0.56	0.58	0.88	0.90	0.98	0.92	0.95	1.00	1.00
K_2O	0.30	1.48	1.05	0.84	1.15	1.87	1.89	1.89	2.10	2.10	1.89
P_2O_5	–	0.14	0.19	3.00	–	0.99	0.49	0.62	0.38	0.33	0.25
H_2O^-	–	4.98	1.37	4.81	–	4.50	2.50	2.58	1.82	2.44	2.18
LOI	2.22	7.20	3.66	46.08	41	25.79	10.48	12.23	13.37	12.01	9.88
S_{total}	–	<0.10	<0.10	1.79	–	0.11	0.17	0.32	0.16	0.37	0.58
CO_2	–	0.22	0.66	2.75	–	1.29	1.32	1.32	0.77	0.66	0.66

Here and in Table 39: Q, quaternary sediments of Russian Plain (Ronov et al., 1963); BS, background soils; BA, background channel alluvium; SS, sewage sludge generated at Saransk treatment facilities; WS, wastewater SPM; TS, technogenic silt.

Petrochemical Features of Technogenic Silts

The chemical composition of background channel alluvium of the Insar River (Republic of Mordovia) is naturally close to that of the background soils and Quaternary sediments of the Russian Plain (Table 38) (Yanin, 2002c, 2011). Appreciable differences are manifested in higher contents of calcium and magnesium oxides and in a smaller amount of potassium and manganese oxides in Quaternary sediments, as well as in elevated iron oxide concentrations in alluvium and organic matter in soils. Compared to soils, alluvium is enriched in silica (the presence of stable quartz), calcium oxide, and carbonates (crushed carbonate rocks); it is depleted in alumina and titanium dioxide (due to the low clay mineral content) and contains less bound water.

The petrochemical composition of technogenic silts widespread in the Insar channel sharply differs from the composition of background alluvium and is relatively stable in the vertical profile (Yanin, 2002c, 2007c). An exception is the upper silt layer (0–20 cm), which is characterized by high levels of organic matter, calcium oxide, unbound water, and a low silica content. Downsection, an increase in sulfur content and decrease in CaO and bicarbonates are observed; P_2O_5 and FeO show a nonuniform distribution. The petrochemical origin of silts is also stably maintained downstream. Changes are manifested as an increase in the share of SiO_2 and a decrease in the amount of organic matter and Al_2O_3, mainly related to hydrodynamic factors contributing to the accumulation of sand fractions in the channel, as well as with diagenetic processes that cause the breakdown of aluminosilicates and new mineral formations, and the transformation of freshly precipitated Fe, Al, Mn hydroxides. At the end of the studied area, due to dilution of technogenic material, natural matter in the silt composition is dominated by sand fractions and SiO_2, the values of the Fe oxidation index increase, and the organic matter content, Al_2O_3, total sulfur, and TiO_2 decreases. The content and characteristics of the component ratios in the petrochemical composition of silts differ from background alluvium by a smaller amount of SiO_2 and an increase in the content of organic matter, Al_2O_3, Ca and Fe oxides, Fe oxide, bicarbonates, etc. Compared to SS, silts have a higher content of SiO_2 and Al_2O_3 and a smaller organic matter content. It can be said that, in chemical composition, silts occupy a peculiar intermediate position between SS and background alluvium.

The petrochemical moduli indicate that the material basis of silts is sedimentary material coming from urban wastewater treatment plants (Table 39). Thus, close modulus values are noted, on the one hand, for technogenic formations, and on the other, for alluvium, soils, and Quaternary sediments. The values of the moduli (hydrolysate, aluminosilicate, maturity, siliceous) reflecting the ratio of the main components of these two sediment groups are very close. The uniqueness of the silt composition is maintained throughout the studied segment of the river. The enrichment of technogenic formations in Fe compounds is reflected in higher values as the femic, ferric, and iron content indices. Technogenic sediments are distinguished from soil and alluvium by a lower oxidation rate and, accordingly, by increased values of the protoxidic modulus. In total mass, the silts are characterized by a predominant reducing setting, although they contain horizons relatively enriched in oxygen. In natural formations, Al is leached from sand fractions by weathering (reflected in lower values of the aluminosilicate modulus). Increased calcareous (compared to soils and alluvium) precipitation and sewage and silt SPM is emphasized by a high plagioclase modulus. The increased values of aluminosilicate and plagioclase moduli, the maturity index of the rock material of source areas, and lower values of the potassium modulus and maturity index indicate that technogenic formations are enriched in clays and aluminosilicates, whereas alluvium, soil, and Quaternary sediments can be characterized as silicites (modulus <0.1) based on the values of the hydrolysate modulus; SS and silts, as weak clayey silicates; and SS, as clay silicites. Higher values of the hydrolysate modulus in silts (compared with SS) indicate active physicochemical transformations of technogenic material during sedimentation and redeposition, and its dilution with natural matter.

Geochemically, silts are a highly nonequilibrium and therefore unstable physicochemical system capable of diagenetic transformations. It is noteworthy that for silts, with distance from the city, the values of the maturity index (after Pettijohn) increase and the maturity index of the rock material in the source areas, on the contrary, decreases. At the same time, the degree of differentiation of material making up the silt increases. Silt enrichment in SiO_2 with distance from the city is reflected in an increased aluminosilicate modulus. Changes in the values of other moduli, especially within area XII, as a rule, are also oriented toward values close to those of background alluvium. All this results from the physicochemical equilibration processes of such a complex and multicomponent system as technogenic silts.

Technogenic silts widespread in the Pakhra River in the zone of influence of Podolsk and its tributaries in the zones of influence of industrial and agricultural sites also differ from typical (background) channel alluvium in their petrochemical composition, which is manifested as a decrease in the amount of silica and an increase in the levels of alumina, sulfur, iron compounds, calcium and phosphorus oxides, fluorine, and organic matter (Table 40) (Yanin, 2004a). The chemical uniqueness of technogenic silts is well emphasized by the petrochemical moduli values (Table 41).

Thus, the increased calcareous content of silts is reflected in the high values of the plagioclase modulus and carbonate content index (a consequence of application of the corresponding compounds at a sewage treatment plant). Higher values of the aluminosilicate and plagioclase moduli, the maturity index of the rock material of the source areas, and lower (than for the background alluvium) maturity index values indicate relative enrichment of silts in clays and detrital aluminosilicates; high values indicate enrichment in organic matter and carbonates. Iron enrichment of silts is reflected by the values of mafic and titanium moduli.

Background alluvium of the Nura River is characterized by predominant silica and a low organic matter content; the composition of alluvium is quite spatially stable. In technogenic silts, the share of silica decreases significantly (up to 40–50%), the contents of other components increase, and high amounts of sulfur are present; the organic matter content sharply increases; extremely high concentrations of mercury are observed (Yanin, 1989, 2004b) (Table 42). The morphological features and petrochemical uniqueness of technogenic silts in the zones of influence of various pollution sources are retained in riverbeds at considerable distances. Thus, even at a considerable distance from Temirtau, their composition is almost identical to that of silts near the city. Obvious differences naturally manifest themselves in an increase in the amount of silica and in a decrease in the content of alumina, calcium oxides, organic matter, and mercury concentrations. The chemical composition (with some variation) of silts in the lower part of their sequence is somewhat different from that of the upper layers, which is a result of their transformation during consolidation and alteration by various diagenetic processes. In particular, the content of silica and iron, manganese, magnesium, sodium, and phosphorus compounds increases somewhat; the amounts of sulfur, fluorine, organic matter, and calcium decrease.

Thus, the petrochemical composition of background alluvium is close to that of the Quaternary sediments and soils that make up the catchment basins, dominated by silica (75–82%) and alumina (4.5–11.5%). This results from the mineral composition (predominance of quartz, presence of feldspars) and the formation of lithogenic alluvium facies. Elevated concentrations of calcium, magnesium, and phosphorus result from the presence of limestone and dolomite (Pakhra) within the catchment area; elevated sodium contents result from soil salinity processes (Nura). Geochemically, background alluvium that has been in the metastable conditions of the oxidation zone for a long time is a mature, relatively stable formation, characterized by a higher degree of differentiation of the material it consists of. The petrochemical composition of technogenic silts is unique and close to the

Table 39. Petrochemical moduli of various sediments

Modulus	Q	OP	F	SS	WS	Technogenic silts, layer, cm; area VI					
						0–20	20–60	60–120	120–180	180–240	240–300
Hydrolysate ($Al_2O_3 + TiO_2 + Fe_2O_3 + FeO/SiO_2$)	0.08	0.08	0.07	0.14	0.27	0.22	0.15	0.18	0.20	0.18	0.15
Aluminosilicate (Al_2O_3/SiO_2)	0.05	0.05	0.04	0.12	0.12	0.13	0.10	0.11	0.11	0.11	0.09
Potassium (K_2O/Al_2O_3)	0.05	0.25	0.23	0.20	0.23	0.20	0.19	0.18	0.20	0.21	0.20
Plagioclase ($Na_2O + CaO/K_2O$	33	1.1	2	16	13	4.5	2.8	2.8	2.2	1.3	1.5
Maturity, after Pettijohn (SiO_2/Al_2O_3)	19	19.4	26.5	8.6	8.7	7.5	10.1	9	8.9	9.5	11
Degrees of differentiation ($SiO_2/K_2O + Na_2O$)	153	50	66	21	17	21	29	28	26	26	30
Maturity of rock material of source area ($Al_2O_3/SiO_2 + MgO + K_2O + Na_2O$)	0.05	0.05	0.04	0.10	0.10	0.12	0.09	0.11	0.11	0.10	0.09
Protoxitic (FeO/Fe_2O_3)	0.99	0.40	0.30	6.6	1.7	1.8	0.7	1.6	2.1	1.1	0.6
Oxidation (Fe_2O_3/FeO)	1.02	2.4	3.3	0.2	0.6	0.6	1.4	0.6	0.5	0.9	1.7
Femic ($FeO + Fe_2O_3 + MgO/SiO_2$)	0.06	0.03	0.03	0.21	0.27	0.11	0.07	0.07	0.11	0.09	0.07
Ferric ($Fe_2O_3 + FeO + MnO/TiO_2 + Al_2O_3$)	0.38	0.37	0.60	0.99	1.19	0.54	0.41	0.53	0.66	0.55	0.50
Fe content ($FeO + Fe_2O_3/MgO$)	0.53	1.34	3.67	1.38	1.26	2.53	1.56	6.95	2.93	2.35	2.50
$Fe_2O_3 + FeO/SiO_2$	0.02	0.02	0.02	0.12	0.15	0.08	0.04	0.06	0.08	0.06	0.05
LOI/SiO_2	0.03	0.1	0.04	1.9	1.5	0.6	0.2	0.2	0.2	0.2	0.15
Silicon (SiO_2/R_2O_3	15.8	15.5	17.8	7.6	5.9	6.2	8	7.4	7.3	7.4	8.3
$SiO_2/R_2O_3 + RO + R_2O$)	4.9	8.4	10.3	1.4	1.3	2.5	2.9	3.7	3.3	3.9	4.7
Calcite content (CaO/MgO)	1.9	0.5	1.6	4.1	2.6	3.3	1.4	4.5	1.2	0.5	0.6
Manganese ($MnO/FeO + Fe_2O_3$)	0.017	0.132	0.024	0.008	–	0.008	0.017	0.013	0.01	0.011	0.011

Table 40. Chemical composition of Pakhra River sediment, %

Component	Background alluvium	Above Podolsk (sands)	2 km below Cherny Creek (silt)	9 km below Cherny Creek (silt)
SiO_2	78.50	77.03	61.70	69.70
TiO_2	0.48	0.43	0.38	0.22
Al_2O_3	4.52	5.74	8.63	7.43
$FeO + Fe_2O_3$	2.62	2.43	4.90	2.94
MnO	0.07	0.06	0.02	0.03
MgO	1.26	1.12	0.66	0.50
CaO	3.17	4.30	6.08	5.73
Na_2O	0.72	0.77	0.68	0.57
K_2O	1.60	1.73	1.62	1.12
P_2O_5	0.26	0.25	0.58	0.39
H_2O^-	0.83	0.65	0.96	0.44
H_2O^+	2.88	2.58	3.72	2.62
S_{total}	<0.01	0.01	0.18	0.06
LOI	2.16	1.88	10.88	9.20
CO_2	2.05	3.37	3.18	1.82
C_{org}	1.20	0.65	4.35	1.97

Table 41. Petrochemical moduli of Pakhra River bottom sediments*

Component	Background alluvium	2 km below Cherny Creek (silt)	9 km below Cherny Creek (silt)
Aluminosilicate (Al_2O_3/SiO_2)	0.034	0.082	0.063
Titanium (TiO_2/Al_2O_3)	0.13	0.06	0.04
Potassium (K_2O/Al_2O_3)	0.39	0.20	0.17
Plagioclase ($Na_2O + CaO/K_2O$)	4.1	6.9	9.2
Maturity, after Pettijohn (SiO_2/Al_2O_3)	29.6	12.2	15.8
Rock maturity ($Al_2O_3/SiO_2 + MgO + K_2O + Na_2O$)	0.032	0.079	0.061
Organosilicate (LOI/SiO_2)	0.03	0.18	0.13
Carbonate content (CaO/MgO)	1.9	6.7	8.5
Al_2O_3/Na_2O (Vogt)	3.9	7.8	7.8
Sodium (Na_2O/Al_2O_3)	0.26	0.13	0.13
$CaO + Na_2O + K_2O/Al_2O_3$	2	1.6	1.7
Gottini index (Al_2O_3–Na_2O/TiO_2)	8.1	20.9	31.2
Mafic ($FeO + Fe_2O_3/MgO + FeO + Fe_2O_3$)	0.67	0.88	0.86
Titanium ($TiO_2/FeO + Fe_2O_3 \times 100$)	18	7.8	7.5

* Calculated based on data of Table 40.

composition of SS generated at treatment plants—the main source of technogenic sedimentary material in industrial–urbanized areas. Sludge has a lower silica content; high contents of organic matter, CaO (and, accordingly, CO_2 carbonates), Al_2O_3, R_2O_5, sulfur; and elevated iron and titanium concentrations. The silica content in silts is often reduced to 42–62%, and there is a significant increase in the amount of organic matter (the LOI indices of silts are 10–26% or more vs. 1.67–3.6% in background alluvium) and calcium oxides (from 0.8–3.6% in background alluvium to 6–10% or more in silts). Technogenic silts are immature

Table 42. Chemical composition of Nura River in zone of influence of Temirtau (0–30 cm layer), %

Component	Background alluvium	Technogenic silts below main wastewater canal, km			
		4.4	9	44.5	105
SiO_2	74.90	42.37	50.46	50.5	57.6
TiO_2	0.24	0.40	0.75	0.68	0.58
Al_2O_3	11.66	17.26	16.96	12.95	11.12
Fe_2O_3	1.28	1.41	1.27	3.04	2.4
FeO	1.41	3.45	4.31	2.16	2.87
MnO	0.06	0.09	0.09	0.38	0.21
CaO	1.35	10.51	4.48	5.92	3.84
MgO	0.62	0.70	1.30	1.9	1.9
Na_2O	2.94	0.50	1.0	1.0	1.35
K_2O	3.36	1.00	1.9	2.05	2.1
P_2O_5	0.07	0.34	0.27	0.29	0.13
H_2O^-	0.26	0.68	1.68	4.04	2.42
LOI*	1.73	19.60	14.39	14.94	12.65
S_{total}	<0.1	0.54	0.83	0.81	0.23
CO_2	0.13	6.38	1.98	4.4	1.54
F	0.02	0.05	0.025	0.05	0.03
Hg, mg/kg	0.044	200	200	10	1.2

formations, and the time in which they form (from the geological viewpoint) is short; they are distinguished by low degrees of differentiation and the ability of active diagenetic changes in the matter they consist of, which substantially determines the fate of the associated organic and inorganic pollutants. Studying the petrochemical composition of sediments and calculating the corresponding indicators (petrochemical moduli) make it possible to identify technogenic silts and more accurately outline the spatial position of the associated technogenic pollution zones in river channels, as well as their most important physicochemical features: concentrators and carriers of the main pollutants entering rivers. From this viewpoint, it is particularly effective to use such petrochemical parameters as the hydrolysate, plagioclase, degrees of differentiation, oxidation, organosilicate, and silica moduli for such purposes, as well as the absolute contents of silica, alumina, calcium oxides, sulfur, and LOI index (which reflects the organic matter content).

Organic Matter in Technogenic Silts

The most important component of river sediments is organic matter (OM), the composition of which in areas of technogenic pollution (with an appreciable increase in specific content) undergoes significant changes. Analysis of the literature data shows that, in practice, the accumulation intensity of individual organic compounds in river sediments is usually estimated (Yanin, 2006b). The group composition of organic matter in river sediments, especially under technogenic conditions, is poorly studied. At the same time, this is the factor that largely determines the physicochemical environmental conditions of alluvial sedimentation and the direction and intensity of various geochemical, biochemical, and physical processes therein (Nikanorov and Stradomskaya, 2006; Matthess, 1984). It can be suggested that the ratio of the main groups of organic agents characteristic of river sediments in areas of technogenic pollution can differ from that in natural (background) conditions. This was first pointed out by V.I. Vernadsky (1960), who noted that one of the dramatic geochemical changes introduced by anthropogenic activity in natural waters is a change in the composition of their organic components, which is manifested not only as an increase in the total OM content, but also the transformation of its qualitative structure.

The group composition of OM in channel sediments was studied on the Pakhra River near Podolsk, a large industrial center in Moscow oblast (Yanin, 2013). Sediments (0–20 cm layer) were collected with TBG-1 corer at the following reference areas of the Pakhra (Fig. 21): II, at the entrance to the city of Podolsk; III, the city center; V–VIII and X, respectively, 2, 2.2, 2.4, 9, and 15 km below the mouth of Cherny Creek; area B, the headwaters of the river (local background). Within each reference area near a given point (2–3 m from the waterline), at least three particular samples (of visually similar sedimentary material) were collected, from which a common sample was formed (~1 L in volume). Samples of sediments were dried in air (in shade), the material of each sample was thoroughly mixed, sifted through a sieve (1 mm), and quartered in order to select charges for subsequent analyzes. For the sequential extraction of organic matter from the main groups of sediments, the following phase analysis scheme was used: (1) Alcohol–benzene mixture (1 : 1 by volume C_2H_5OH and C_6H_6, extraction in a Soxhlet apparatus for 20 h at room temperature). It is believed that this extracts mainly lipids (fats, waxes, resins) from sediments (Kononova, 1963). (2) Sodium pyrophosphate solution (0.1 M $Na_2P_2O_7 \cdot 10H_2O$ with the addition of 0.1 *n* NaOH, extraction for 12 h, pH ~ 13; the sample was treated three to six times until the solution was completely clear). This extracts mainly humic acids associated with calcium and nonsilicate forms of iron and aluminum from sediments (Kononova and Belchikova, 1961). The separation of humic (HA) and fulvic acids (FA) was carried out according to the method (Ponomareva and Plotnikova, 1968), and organic carbon was determined according to I.V. Tyurin's method in V.P. Tsyplenkova's modification (1963). The amount of organic carbon in the insoluble residue (C_{ROM}, which characterizes residual organic matter, including clay–humus humin, lignin and, under pollution conditions, technogenic organic matter) was calculated by subtracting the total organic carbon in the alcohol–benzene (C_{lip}) and the pyrophosphate (C_{HA} + C_{FA}) extracts from the total organic carbon content (C_{org}) in the sample. The results of all analyses are given for the air-dry mass of the sample.

Background alluvium is characterized by a low organic matter content (C_{org} = 0.65%), which is dominated by humic acids (81.8% C_{org}); the share of residual OM is small (15.4%), and lipids are negligible (1.5%). An increased (in comparison with mobile FA) HA content is typical, which indicates very high humification of OM in background sediments (Table 43).

Technogenic silts differ from background alluvium by a significantly higher (two to four times) total OM content and fundamentally different ratio (balance) of its main groups (Tables 44, 45; Fig. 35).

The specific concentrations of residual OM (3–11 times) and, especially, lipids (6–59 times) increase the most dramatically in silts. In turn, the relative share of lipids in silts increases to 10–20% (vs. 1.5% in alluvium), and residual OM increases to 27.3–48.6% (vs. 15.4%). At the same time, a decrease in the relative share (with a slight increase in specific content) of HAs (from 81.8% in alluvium to 29.6–57.1% in silts) is observed in technogenic silts. With distance from Podolsk, a decrease in the total OM content in silts is observed (as a result of a decrease mainly in the amount of poorly soluble OM and HA), as well as an increase in the specific content and relative fraction of FA. This determines the change in the type of humus and the degree of humification of OM in sediments. Whereas the background alluvium, as noted above, is characterized by very high humification of OM (as a result of its oxidative transformation), which is typical of rivers and reservoirs of the humid zone, silts, especially in their maximum distribution zone (areas V–VII), differ by a lesser degree of OM humification, which points to predominant reducing processes under technogenic conditions. And whereas the background alluvium is characterized by a fulvate–humate type of humus, technogenic silts in the zone nearest source of pollution are a fulvate type of humus (areas III, V); downstream, humate (areas VI, VII); followed by humate–fulvate (areas VIII, X), which obviously reflect the spatial differentiation of the physicochemical conditions and sedimentation processes in the river channel. In particular, it is possible that in the Pakhra River, within the immediate zone of influence of the city (areas VI and VII)—where in silts $C_{FA}/C_{HA} < 1$ and calcium predominates in the composition of absorbed bases—humate humus develops somewhat, i.e., the formation and (to a greater extent) accumulation (as a result of hydraulic sedimentation of wastewater suspension) of the least mobile, stable organomineral derivatives of humic substances: calcium humates.

The uniqueness of the OM composition of technogenic silts and the difference between the latter and the background alluvium are clearly underscored by the values of various geochemical coefficients (Table 46). It is indicative that in silts (as opposed to alluvium and other sediments), the organic carbon concentrations (C_{org}) significantly exceed the carbonate carbon content (C_{carb}). Whereas the C_{carb}/C_{org} ratio in Phanerozoic sediments is 7.5, in the Earth's sedimentosphere, 5.4; in the sedimentary layer of the continental crust, 5.3; in Cenozoic sediments, 2.9 (Ronov and Yaroshevsky, 1976), and in background alluvium, 1.3—in technogenic silts it is, on average, 0.7. This indicates the important role of technogenic silts in the local geochemical organic carbon cycle.

The transformation of the OM composition and increase in its content determine the uniqueness of the elemental composition of technogenic silts, in which the nitrogen, hydrogen and carbon contents increase by many times (compared to background alluvium and podzolic soils) (Table 47). The extremely high concentrations of these components in SS are noteworthy.

It is well known that virtually any phase method for determining the group composition of OM in sedimentary formations is to a certain extent conditional (Alexandrova, 1980; Orlov and Grishina, 1981). However, in our case, it is not so much the exact (qualitative and quantitative) identification of OM present in river sediments that is important, but the established and quite regular tendency toward a sharp increase in total content and a significant change in the structure of the OM group composition of river sediments

Table 43. Group composition of organic matter (OM) of Pakhra channel sediments

Area	C_{org}, % OM	% C_{org}				
		lipids	humic acids			residual OM
			total	FA	GA	
II	1.38	4.4	43.5	22.5	21.0	52.1
III	1.52	6.6	50.0	34.2	15.8	43.4
V	1.71	9.9	32.2	21.1	11.1	57.9
VI	2.46	13.4	36.2	16.3	19.9	50.4
VII	2.60	22.6	29.6	13.1	16.5	47.7
VIII	1.65	20.0	46.7	26.7	20.0	33.3
X	1.26	15.9	57.1	33.3	23.8	27.0
Average (III–X)	1.87	14.7	41.9	24.1	17.9	43.3
Background	0.65	1.5	81.8	39.4	42.4	16.7

Table 44. Intensity of OM concentration in technogenic silts (in concentration ratios with respect to content in background alluvium)

Area	C_{org}	Lipids (C_{lip})	Humic acids			Residual OM (C_{ROM})
			total (C_{HS})	BC (C_{FA})	GC (C_{HA})	
II	2.1	6	1.1	1.2	1	6.5
III	2.3	10	1.4	2	0.9	6.0
V	2.6	17	1.0	1.4	0.7	9.0
VI	3.7	33	1.6	1.5	1.8	11.3
VII	3.9	59	1.4	1.3	1.5	11.3
VIII	2.5	33	1.4	1.7	1.2	5.0
X	1.9	20	1.3	1.6	1.1	3.1
Average (III–X)	2.8	28	1.4	1.6	1.2	7.6

Table 45. Type of humus and degree of humification of OM of Pakhra channel sediments

Area	Type of humus		Degree of humification	
	C_{FA}/C_{HA}	after (Aleksandrova, 1980)	$(C_{HA}/C_{org}) \times 100\%$	after (Orlov and Grishina, 1981)
II	0.93	Fulvate–humate	43.5	Very high
III	0.46	Fulvate	50.0	Very high
V	0.53	Fulvate	32.2	High
VI	1.22	Humate	36.2	High
VII	1.26	Humate	29.6	Average
VIII	0.75	Humate–fulvate	47.7	Very high
X	0.71	Humate–fulvate	57.1	Very high
Background	1.08	Fulvate–humate	81.8	Very high

formed in polluted areas. Thus, the relatively low concentration of C_{org} (0.65%) in the Pakhra's background alluvium is because the latter accumulates in a setting of active hydrodynamic conditions that promote the removal of organic detritus and pelitic particles from sediments and the formation of so-called lithogenic riverbed facies, which is dominated by sand fractions and silica. Apparently, the established content and structure of the group composition of alluvial OM are typical of the natural conditions of small lowland rivers. For example, in sands (even silted) of channel banks in rivers of central regions of the Russian Plain,

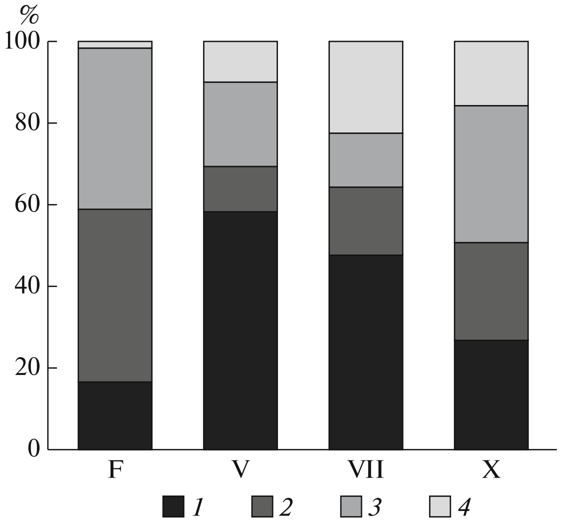

Fig. 35. Group composition of OM of alluvium (F) and technogenic silts (areas V, VII, X): (*1*) residual OM; (*2*) humic acids; (*3*) fulvic acids; (*4*) lipids.

C_{org} varies within 0.11–0.34% (Lazarenko, 1964). According to the data of (Swain, 1970), river sediments in the humid zone contain on average about 1% OM. Based on Vassoevich's estimate (1973), continental sedimentary rocks have an average C_{org} concentration of 0.62%. The qualitative composition of OM in the channel alluvium of small lowland rivers in natural conditions is mainly determined by the input of allochthonous material from the catchment area; autochthonous matter plays a much smaller role. The main sources of OM that can concentrate in sediments of small rivers are catchment soils (the main source of humic acids) (Artemyev, 1993; Pawson et al., 2008); to a lesser extent, plant waste and hydrobionts (the main sources of lipids) (Breger, 1966). The composition of OM of soddy-podzolic soils (C_{org} = 1.2–2.3%) widespread in the Pakhra basin is dominated by humic acids (up to 68–69% of total OM) (Aleksandrova, 1980), which obviously determines their dominance in alluvium. Even in bottom sediments of unpolluted freshwater objects (reservoirs, ponds, lakes), where significant masses of autochthonous nutrients are involved in sedimentogenesis, the share of humic acids (in the composition of which HA usually predominate) reaches 40–70% of total OM (Nikanorov and Stradomskaya 2006). It appears that lipids in alluvium are dominated by stable compounds (hydrocarbons and free fatty acids), the low concentration of which is a consequence of their minor input into the watercourse and reflects the transformation process of labile OM in early diagenesis. Thus, in the arable soddy-podzolic soil horizon, specific lipid concentrations are about 0.1%, which correlates quite well with their low content in background alluvium. The basis of residual OM, the concentration of which in river sediments usually varies from hundredths to several percent (Artemyev, 1993) obviously consists of the decomposition products of lignin and clay–humus humin.

Table 46. Changes in values of various coefficients in Pakhra bottom sediments

Area	C_{carb}/C_{org}	Oxides Fe/C_{org}	Al_2O_3/C_{org}	CaO/C_{org}
II	0.6	1.7	4.9	3.3
III	1.0	2.2	4.5	4.1
V	0.9	1.8	4.1	2.8
VI	0.4	1.2	2.8	2.1
VII	0.3	1.2	2.4	2.1
VIII	0.6	1.8	3.3	3.0
X	0.7	1.7	3.9	3.3
Average (III–XI)	0.7	1.7	3.5	2.9
Background	1.3	3.1	6.7	6.3

Table 47. Elemental composition of various sediments, %

Sampling area	N	H	C_{opr}	C_{carb}	C_{org} : N
SS, Podolsk	2.83	3.23	24.37	0.567	8.6
″, Klimovsk	2.48	3.57	27.68	0.78	11.2
Technogenic silts, Pakhra River, below Cherny Creek	0.41	0.59	5.50	1.745	13.4
Background alluvium	0.06	0.09	0.66	0.027	11.0
Podzolic soil	0.06	0.04	0.64	–	10.7

The amount and structure of the group composition of OM in silts are also regular and primarily due to the specifics of Pakhra source areas with sedimentary material in the zone of influence of Podolsk. As noted above, the material basis of silts is sedimentary material transported into watercourses with industrial and domestic wastewater and SS generated in sewage treatment plants can be considered a peculiar geochemical analog of this material and silts. Based on available data, SS contains benzene substances (up to 50–90% of total OM), fats (7–17%), alpha-cellulose (2–12%), hemicellulose (3–25%) (Evilevich and Evilevich, 1988), and significant amounts of lipids (Payet et al., 1999), and they differ by a low relative content of humic acids (about 20% of the total OM) (Pascual et al., 1997). In household wastewater, the share of humic acids (of the total dissolved OM) is significantly lower (30.1–41.3%) (Manka et al., 1974) than in natural surface waters (60–80%) (Varshal et al., 1979). It is well known that an increase in the specific and relative contents of the group of oxidation-resistant organic compounds is typical of wastewater discharged from city treatment plants. Under pollution conditions in silts, higher fatty acids and petroleum products can accumulate, the decomposition rate of which is low, which leads to an increased content of residual OM in sediments. The formation of Ca, Al, Mn, and Fe humates in silts, which are poorly soluble and highly resistant to microbial decomposition, cannot be excluded. There is a long-standing report on the increase in the amount of oxidation-resistant organic compounds in sediments of polluted watercourses (Bunch et al., 1961). Thus, technogenic sedimentary material transported into rivers with wastewater and surface runoff is characterized by high contents of lipids and hydrolysis-resistant organic matter and a reduced amount of humic acids. This largely determines the uniqueness of the group composition of OM in technogenic silts.

An important component of technogenic silts is petroleum products. Thus, in Pakhra River silts within the city of Podolsk, the content of petroleum products was 350 mg/kg; 2 km lower, 750 mg/kg; 9 km lower, 300 mg/kg, whereas in channel sediments above the city, it did not exceed 5 mg/kg. In Petritsa River silts (Pakhra River basin) in the zone of influence of the village of L'vosky, the concentration of petroleum products ranged from 330 to 9400 mg/kg; of Oranka River (Troitsk), it was 200 mg/kg; of the Svinorye River (Aprelevka), 300 mg/kg; of the Muranikha River (Domodedovo Airport), 630 mg/kg; in Podolsk SS, 16200 mg/kg. Petroleum pollution in the Pakhra River is formed predominantly by oily petroleum products. In silts of the Svinorye, Muranikha, and Oranka rivers, light oil products accumulate; it the Petritsa River, resinous (possibly oxidized). Very high levels of petroleum hydrocarbons (up to 22691 mg/kg) in technogenic silts of the Yekateringofka (Leningrad oblast) have been noted by A.Yu. Guardunov (2005). Even the results of single sampling of many rivers in Moscow oblast indicate a significant content of petroleum products in their channel sediments (up to 500–5100 mg/kg, with a background level of 50 mg/kg). In silts of the Pakhra River and its tributaries, high levels of benzo[a]pyrene (up to 0.55 mg/kg) have also been established. High concentrations of this substance are also characteristic of Podolsk (0.14 mg/kg) and Klimovsk SS (0.15 mg/kg), which indicates its input into wastewater SPM.

Analysis of the literature suggests that SS generated at city treatment plants are significantly enriched in various, first and foremost, pathogenic and conditionally pathogenic microorganisms (Yanin, 2009b). This a priori determines the microbiological uniqueness of technogenic silts, their increased microbiological hazard, and the potential role of these organisms in forming the organic matter composition of these modern channel sediments.

Thus, in background conditions, the organic matter distribution in the channel sediments of a small river is mainly determined by the mechanical differentiation of incoming allochthonous sedimentary material and to a lesser extent by the overlapping process of autochthonous organic matter accumulation. This results in a low organic matter content in the background alluvium ($C_{org} = 0.65\%$) and the prevalence of humic acids in its composition (81.8% C_{org}) with an insignificant share of residual OM (16.7%) and lipids (1.5%). Background alluvium is characterized by the fulvate–humate type of OM and a very high degree of humification, which indicates the predominance of oxidative processes under natural conditions. Overall, in their component composition, background alluvium OM is close to OM of the sedimentary rocks and, especially, soils that make up the catchment area.

Technogenic silts that form in the zone of influence of an industrial city are characterized by a higher organic matter content (C_{org} 1.26–2.60%, average 1.87%); moreover, they have the most sharply increasing specific lipid concentrations (6–59 times compared to background alluvium) and insoluble organic matter (3–11 times). To a much lesser extent (1.3–1.6 times), there is an increase in the specific content of humic acids in which FAs already dominate. Silts differ from background alluvium by a fundamentally different structure of the group composition of their OM: the relative share of lipids increases to 10–20%, residual OM increases to 27.3–48.6%, and humic acids decrease to 29.6–57.1%. In general, OM in technogenic silts is characterized by a medium and high degree of humification and fulvate–humate type of humus, which indicates the predominance of reducing processes under pollution conditions. With distance from the city, the total organic matter content in silts decreases mainly due to a decrease in the amount of humic acids and poorly soluble organic compounds. In technogenic silts, the amount of organic carbon significantly exceeds the carbonate carbon content, which distinguishes them from background alluvium and other sedimentary formations.

Petroleum products and benzo[a]pyrene play an important role in the formation of physical properties, texture, and structure of technogenic silts, as well as their color and odor. Their contents in the most heavily polluted areas reach several hundred mg/kg or more. A certain part of technogenic OM relatively safe for living organisms is capable of transforming into more toxic compounds under river conditions (especially in contaminated areas), which increases the ecotoxicity of technogenic silts. OM concentrating in technogenic silts a priori determines their most important physicochemical properties (including increased cohesion, consolidation, and erosion resistance) and plays an important role in the behavior of many heavy metals and other chemical elements. The high organic matter content in silts causes additional oxygen consumption for its oxidation, which contributes to the formation of anaerobic (gley) conditions in the riverbed, which increase the migration mobility of metals and their exchangeability between sediments and water. Lipids, which are present in significant quantities in technogenic silts and which are the most labile part of chemical agents, can contribute to the formation of mobile, geochemically active forms of metals, and the high content of poorly hydrolyzed organic matter can increase the reserves of their tightly bound forms.

CHEMICAL ELEMENTS IN TECHNOGENIC RIVER SILTS

Bottom sediments of surface watercourses are traditionally used as a component (indicator) to identify the composition, intensity, and scale of technogenic pollution of water systems and landscapes as a whole. This is largely because they, being the most important components of aquatic landscapes, are the last link in local landscape–geochemical interfaces, which is why their material composition reflects the geochemical features of catchment areas. This dependence is especially starkly manifested in the basins of small rivers that receive wastewater and surface runoff from developed territories.

Technogenic Geochemical Anomalies in Bottom Sediments of Rivers of Industrial–Urbanized Areas

The following areas of the river network were investigated within the Moscow region: (1) streams or headwaters of small rivers that receive wastewater discharge; (2) small rivers directly below the source of impact; (3) the channels of medium-sized rivers in areas below a city or below a site of sewage discharge into them (Yanin, 1988, 2002b, 2004a). The length of sampling areas was 250–500 m. Sampling (with a step of 10–20 m) was carried out in places of sediment accumulation visually characterized as technogenic silts (the most common situation; in rare cases, very-fine-grained and fine-grained sands were selected or technogenic fluffy sediments of point bars). The number of samples in each set characterizing the source of pollution varied from 30 to 40. Streams in the upper reaches of the Pakhra River (85 samples) were studied as the background.

The qualitative composition of the established geochemical associations as a whole weakly reflects the specifics of a particular technogenic pollution source (city, industrial zone, enterprise, factory), since the same elements accumulate in the bottom sediments of many studied watercourses (Tables 48, 49).

Ag and Hg are the leading elements in the technogenic geochemical associations in bottom sediments (technogenic silts) in the studied rivers. Often the associations also include Cd and Cu; sometimes Zn and Bi; rarely Sn, Pb, Mo, W; and very rarely, Hf, B, Nb, and Ce. Usually, elements of different toxicity (Hg, Ag, Cd, Sn, Bi, Sb, W, Mo, Pb, Zn, Cu, Ni) accumulate most heavily in silts, with contents tens, hundreds, and sometimes thousands of times higher than background levels. In general, it can be assumed that for the Moscow region, Ag, Hg, and Cu play a leading role in the scale of technogenic pollution of watercourses, followed by Zn, Sn, Ni, Cd, Pb, Cr, and in rare cases, Bi, P, Mo, W. Usually, the association of a specific object (city, industrial zone, plant) has an individual manifestation, primarily in different quantitative ratios of the same elements belonging to different associations (i.e., in their position in K_C value range). Frequently, a qualitative depletion is observed in the composition of associations (a decrease in the N_E values) for impact sources that use “monomineralic raw materials” in the production cycle. This is typical of the zones of influence of textile–weaving, machine-building, and food industry enterprises (N_E = 5–11), as well as objects where elements enter as undesirable impurities in the composition of raw materials (e.g., brick and ceramic tile factories, N_E = 12–14). Severny Creek (Domodedovo) is characterized by the occurrence of Ce. The impact of the ceramic tile plant is unique (the lead role is played by Hf, B, Hg; Zn, Zr, Sr, Pb, Ba, and Cu are also present). There is an indubitable specificity of Bi (in terms of concentration intensity) for the zones of influence of scientific centers (pilot production enterprises with an electronics and radio engineering profile) and airports (mechanical repair), as well as Cr for the latter. The high Sn content in sediments of the Konopelka, which drains the territory of the Shcherbinsky landfill, is due to waste disposal from a tin plant. Associations characteristic of multifunctional industrial zones, for chemical and radio engineering enterprises, and nonferrous metallurgy plants, as a rule, are distinguished by maximum N_E values of 18–26. In this group of objects, the multifunctional sites of Podolsk and

Table 48. Technogenic geochemical associations in bottom sediments of streams in Pakhra basin

Industrial load	City	River, stream	Order of K_C values of chemical elements					N_E	Z_C	Z_{ST}
			>100	100–30	30–10	10–3	3–1.5			
Integrated production	Podolsk	Cherny	Hg_{317}–Ag_{150}	Cd_{60}–In_{53}	Cu_{26}–Ni_{24}–Pb_{22}–Sn_{15}–Sb_{14}–Se_{11}	V–Zn–Cr–Nb–P–W–As–Bi–Sr–Ba	Co–Be–Mo–Sc–F–Y	26	730	585
	Domodedovo	Severny	–	Ag_{44}	Cd_{14}–Ce_{12}	Zn–Se–Hg–Sb–Sn–As–Pb	P–Cu–Sc–Sr–Ti–Co–Bi–Ni–Ba	19	105	79
Chemical industry	Butovo	Gvozdyanka	–	–	Hg_{26}	Sn–Ag–Sc–Cr–Ga–P–Pb–Mo	Ti–Co–Nb–Cu–Ba–V–Sr–Sc–As–F	19	70	42
	Aprelevka	Svinorye	Hg_{553}–Ag_{107}	Ni_{35}	Cd_{25}–Sr_{20}	Cu	Pb–As–Se–Co–Bi	11	745	705
	Podolsk	Khudozhestvennyi	–	–	Sn_{13}	Ag–Cd–Cu–Ba–Co–Hg	Zr–Pb–Ni–ScTi–V–Zn–Sr–P	16	46	18
Production of building materials	Podolsk	Plescheevsky	–	–	Ag_{14}	Hg–Cu–Ba–Pb–Co–P–Sr	Cd–Sc–Ni–V–Li–Zn–Ti–Ga–F	17	51	30
	Domodedovo	Promyshlenny	–	–	Ag_{25}–Hg_{12}–Zn_{11}	Bi–Sr–Cu–Zn–Sc–Sn	Pb–Ga–Mo–Cr–P–F	15	76	46
Machine building	Podolsk	Bolnichny	Hg_{409}	Ag_{46}	–	Zn–Sr–Pb–Bi–Sc–Ba–Cd	Cu–Y–Co–Ni–Li–Cr–As–Se	17	490	470
Vtortsvetmet	L’vovsky	Petritsa	Hg_{180}–Ag_{170}	Pb_{34}–Bi_{33}	P_{14}–Cu_{12}–Zn_{11}	Sb–Sn–Ba–Cd–F	Co–Ga–Cr–Sr–As	17	473	430
	Shcherbinka	Visensky	Ag_{457}–Hg_{399}	–	Cu_{17}	Cd–Zn–Bi–P–Sr–Cr–Ni	Ba–Co–Pb–Sc–Zr–Mo–As–Se	18	907	869
Coke chemistry	Vidnoye	Kupelinka	–	–	Hg_{15}	Zn–Mo–Cu–Sr	Ni–Ag–Co–Nb–Sc–Li–Cr–Cd	13	39	23
Legkaya	Trinity	Desna	–	–	–	Sn–Ag–Mo–	Sr–Ni–Zn–Mn–Hg–Be–Cu–Cd	11	21	13
Science Centers	Troitsk	Oranka	Ag_{198}	Cd_{44}	Hg_{15}	Bi–Cu–Zn–P–Sn–Pb	Sr–Co–Ni–Ba–Sc–Cr–F–As–Se	18	288	270
	Research Institute of Communications	Neznayka	Ag_{210}	Bi_{56}–Hg_{43}	P_{14}	Zn–Cu–Cr–Sc–Cd	Y–Sn–Ga–Nb–Ti–Zr–Yb–Sr–Mn–Ni–Co–Se–As–F	23	354	310
Airports	Domodedovo	Muranikha	–	Ag_{46}	Hg_{29}	Bi–P–Cu–Mo–Zn–Cr–Ga	Nb–Ni–Co–Ti–Zr–Y–Sn–Cd	17	110	88
	Vnukovo	Likovo	Ag_{1250}–Bi_{100}	Cr_{49}	Ba_{27}–Cu_{18}–Zn_{17}–Sn_{14}–Ag_{13}	Pb–Cd–	Ni–Mn–Sr–P–Ga–Nb–Sn–Y–Ti	19	1498	1400
Shcherbinsky landfill		Konopelka	Ag_{232}–Sn_{151}	Cd_{64}–Ni_{56}	Sb_{16}–Cu_{11}	Hg–Pb–Zn–Cr–	Co–Sc–Zr–Ba–As–Mn–Ba–Sr	18	550	330

Table 49. Technogenic geochemical associations in bottom sediments of watercourses in Moscow oblast

City, watercourse, industry, factory	Order of K_C values of chemical elements					N_E	Z_C	Z_{ST}
	>100	100–30	30–10	10–3	3–1.5			
Schelkovo, Klyazma River, textile, chemical, metalworking, electronics, etc.	Ag_{921}–Hg_{398}	Bi_{48}–Zn_{44}–Cu_{38}–Ni_{36}–P_{31}	Cd_{17}–Sn_{14}–Cr_{11}	Sr–Pb–Ba–Co	W–Mo–V–Mn	18	1570	1395
Obukhovo, Klyazma River, below Schelkovo	Ag_{141}	–	Hg–Cu	P–Cr–Bi–Co–Sn–Cd–Ba	Ni–V–Mo–Sr	14	209	178
Noginsk, Klyazma River, below mouth of Lavrovka River, textile, mechanical engineering, construction industry	Ag_{380}	Zn_{43}–Mo_{42}–Cu_{31}–Cd_{30}	$(Sn–Mn)_{22}$–Ni_{19}–Cr_{15}–Pb_{11}	W–Co–V	B	14	829	469
Noginsk, Klyazma River, below city	Ag_{125}	–	Zn–Cd	Cu–Cr–Sn–W–Ni–Co	Mo–Pb–Mn	12	371	340
Elektrostal, Vokhonka River, metallurgy, mechanical engineering, construction industry	Ag_{220}–W_{220}–Mo_{110}	Ni_{92}–Cu_{34}–Zn_{33}	Pb_{20}	Sn–Cr–Cd–Co–V–Mn	B	14	748	572
Kolomna, Moscow River, heavy engineering, construction industry	–	Ag_{66}	Cu_{11}	Zn–P–Hg–Pb–Cr–Ni–Ba–Co–F	V–Sn–Sr–Mo	15	116	82
Dmitrov, stream, excavator plant	–	Hg_{37}	–	Pb–Ag–Sr–Ba	Cu–Zn–Mo–Mn	9	57	54
Dmitrov, stream, construction industry	–	–	Mo_{12}–Nb_{11}	Ag	Ba–Pb–Cu–Mn–Sr–Co–V–Ga	11	34	28
Voskresensk, Moscow River, chemical, construction industry	–	Ag_{33}–Hg_{31}	Cu_{17}	Zn–Sr–Sn–P–Pb	Bi–Ba–Cr–Co–Mo	13	104	70
Volokolamsk, Lama River, textile	–	Hg_{53}–Ag_{52}	Bi_{19}	Cu–W–Ba–Pb–Zn–P–Sn	Sr–Mo–Co–V–Cr–Ni	16	156	137
Vysokovsk, Vyaz River, weaving	–	–	Ag_{22}–Hg_{21}–Cu_{12}	Zn–Ba–Pb	Sr–Co–Sn–Mo–Cr–P	12	71	53
Khorlovo, stream, technical fabrics	–	–	–	Ag	P–Nb–Cu–Pb	5	9	7
Vereya, Protva River, sewing	–	–	–	Ag	P–Ba–Sr–Mo–Cu–Nb–Pb	8	12	9
Zaraysk, Osyotr River, spinning–weaving, shoe, feather products	–	–	–	P–Ag	Cu–Co–Nb–Pb	6	13	7
Karasevo, stream, brick factory	–	Hg_{35}	Ag_{28}	Cu–Ba–V–Co	Ni–Zn–P–Ga–Sr–Pb–Mn–Cr	14	86	69
Katuar, creek, ceramic tile factory	–	Hf_{43}	B_{19}–Hg_{17}	Zn–Zr–Sr–Pb–Ba–Cu	Ag–Co–Ga	12	104	44
Lotoshino, agricultural products processing	–	–	–	Ag–Ba–Cu–P	Co–V–Cr–Ga–Pb–Mo–Ni	11	24	11

Shchelkovo stand out. They differ in the specifics of the industries located there, but they are similar in that those enterprises are widely involved in the production cycles of multielement raw materials, chemical processes, metal plating, metal processing, etc. This is reflected in high N_E and K_C values of many elements. Nevertheless, the geochemical associations established in the zones of influence of these cities differ in their appearance and structure. Thus, in the area of Podolsk (Cherny Creek), there is heavy accumulation of indium, antimony, selenium, and niobium in silts, which is not typical of the Schhelkovo's zone of influence; it is more significant than the cadmium, lead, arsenic, and vanadium concentrations in Klyazma River silts. In turn, Klyazma silts are distinguished by a sharp accumulation of silver, mercury, bismuth, zinc, phosphorus, and strontium. Assessment of the associations shows that an extremely high level of technogenic pollution and an extreme degree of sanitary–toxicological hazard are characteristic of watercourses in the zones of influence of Podolsk (Cherny and Bolnichny creeks), Aprelevka (Svinorye River), the village of L'vosky (Petritsa River), Shcherbinka (Vissensky Creek), the Communications Research Institute (Neznayka River), Vnukovo Airport (Likovo River), Shchelkovo and Noginsk (Klyazma River), Elektrostal (Vokhonka River), and the Scherbinsky landfill (Konopelka River). A very high pollution level and extreme degree of sanitary–toxicological hazard have been established for the zone of influence of Troitsk (Oranka Creek). A heavy concentration of Hg, Ag, and Pb in technogenic silts was noted for northwestern Russian rivers (Opekunov, 2005). It cannot be excluded that for industrial areas, platinum metals (Yanin, 2008c), as well as technogenic radionuclides unrelated to nuclear tests and the nuclear fuel cycle (Yanin, 2017b), are typical elements of geochemical associations recorded in river bottom sediments.

Thus, the impact of various objects (city, town, industrial zone, plant, factory) causes the accumulation of qualitatively similar geochemical associations in bottom sediments of waterbodies, which almost always include a wide group of elements: Hg, Ag, Cd, Co, Cu, Ba, Zn, Cr, P, Sc, Sr. In most cases, highly toxic chalcophile elements are distinguished by the highest K_C values. Virtually every geochemical association has a certain specificity, which usually manifests itself in the concentration intensity, less frequently in the occurrence of elements characteristic of only a particular object.

Features of the Spatial Distribution of Chemical Elements in River Sediments

Studying the spatial features of the chemical element distribution in river bottom sediments makes it possible to assess the range of influence of pollution sources, to identify geochemical barriers, to establish the spatial ratio of the contents of various chemical elements due to differences in their migration intensity and supply sources, and to estimate the probability of technogenic impact on next-order watercourse and on the studied river basin as a whole.

Moscow region. In the Pakhra River basin, the spatial distribution of chemical elements in river sediments in the zones of influence of various pollution sources is governed by the type of technogenic impact, the characteristics of pollutant supply to watercourses, and the geomorphological and hydrological parameters of the latter (Yanin, 1988, 2004a). The material presented below is based on a geochemical survey of technogenic silts with a 250 m sampling step (their upper, relatively lithified horizon was assayed) in an area of different objects. In small streams, the sampling sites (up to 50–100 m) were more densely clustered.

In the zone of influence of Podolsk, an important feature of the spatial distribution of chemical elements in silts is significant variation in their concentrations downstream (Fig. 36). It is most pronounced for the leading elements of the association—Ag, Sn, Hg, Cd, Pb, Ni; to a lesser extent, for Cr, Cu, Zn. Elements differing by a lesser concentration in sediments are characterized by a relatively uniform distribution (Co, P, V, Sr, etc.). Based on the pollution sources and features of the spatial (lateral) distribution of elements in channel sediments within the studied segment of the Pakhra, the following areas were distinguished (Table 50 (1) Area 1, from the upper border of Podolsk to the Pakhra's confluence with Belyaevsky Creek—within this area, surface runoff from a nonindustrial suburb enters the river. (2) Area 2, from the mouth of Belyaevsky Creek, which receives surface runoff from a Podolsk residential district, to Bolnichny Creek. (3) Area 3, from the mouth of Bolnichny Creek to Cherny Creek, where old residential buildings and a large industrial area are situated; the main influx of pollutants is transported by wastewater along Bolnichny Creek and with surface runoff from urban areas. (4) Area 4, from the mouth of Cherny Creek to the village of Pokrov, where many enterprises are located, wastewater of which enters the Pakhra via streams; the main volume of wastewater in Podolsk (from its treatment facilities) enters the Pakhra via Cherny Creek. (5) Area 5, from Pokrov to the mouth of the Kanopelka River, i.e., to the Shcherbinsky landfill. (6) Area 6, from the mouth of the Konopelka River to the mouth of the Rozhaya River, located in the zone of influence of the Shcherbinsky landfill. (7) Area 7, below the mouth of the Rozhaya River, in which Severny Creek receives wastewater from Domodedovo.

Within areas 1 and 2, the Pakhra's channel is covered with low-silty sandy sediments, similar in morphology to background alluvium. Technogenic fluffy layers and small silt lenses are encountered sporadically only near the waterline. Subsequent segments of the Pakhra's channel are distinguished by heavy development of technogenic silt and fluffy-layer accumula-

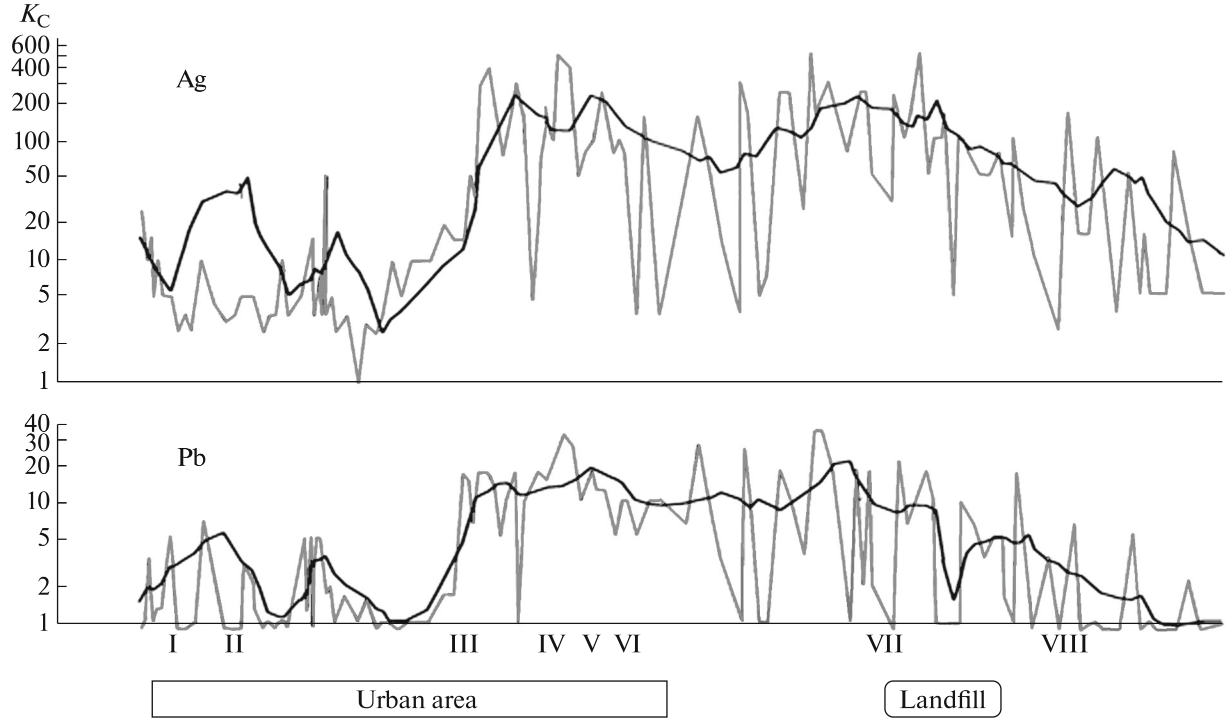

Fig. 36. Silver and lead in Pakhra River channel deposits in zone of influence of Podolsk. Places where main tributaries flow into Pakhra: I, Belyaevsky Creek; II, Bolnichny Creek; III, Cherny Creek; IV. Pleshchevsky Creek; V, Khudozhestvenny Creek; VI, Visensky Creek; VII, Konopelka River; VIII, Rozhaya River; thin line, actual distribution; bold line, distribution curve for smoothed data; K_C, concentration coefficient.

tion zones. The vertical thickness of silts, e.g., within areas 4 and 5, sometimes reaches 1–1.2 m; point bars are composed of technogenic fluffy layers for almost their entire length. Technogenic silts are widespread in creeks (Bolnichny, Cherny, Visensky, Khudozhestvenny, Plescheevsky, etc.), which receive runoff from the main industrial zones, as well as in reservoirs and streams that drained the Shcherbinsky landfill (before its reclamation).

The river bottom sediments within area 1 are mainly characterized by low (with respect to the background) chemical element contents. Exceptions are Ag (K_C up to 8–9) and Hg (K_C up to 7), which (along with Pb) show a higher variation in their contents and certain correlations, which obviously indicates a single source of their influx into the river. The low pollution level of the watercourse recorded by sediments within the studied area is formed mainly by the inflow of surface runoff from the city (lead) and runoff from the village of Dubrovitsa (Hg, Ag, and Cu input may be associated with the large cattle-breeding farm located here).

Within river sediments in Area 2, the levels of many chemical elements increase markedly, with their maximum concentrations occurring at the mouth of Belyaevsky Creek, along which surface runoff polluted by industrial emissions and automobile exhaust flows from the urban area. The inhomogeneity of the spatial distribution of elements also increases substantially. Here, Ag and Hg, as well as Pb, and to a lesser extent Co, Cu, Ni, Zn anomalies were also the most pronounced. Relatively high Sr and P concentrations are apparently due to natural factors (limestone and dolomite outcrops). In the general case, the geochemical anomalies are small in extent: in the first few hundred meters below the mouth of the stream, the concentration of most elements already decreases to the background level. A high degree of correlation is observed for the spatial distribution of the leading elements of the established geochemical association. This indicates a single source of input (mainly in runoff along Belyaevsky Creek) and similar migration and accumulation mechanisms. It is significant that for Mo and V (weakly accumulating elements in deposits), a rather pronounced negative correlation with the group of leading pollutants is recorded (Table 51).

Within Area 3, the bulk of technogenic sediment enters the river via Bolnichny Creek. Hg (K_C = 403), Ag (46), and to a lesser extent Zn, Sr, Pb, Bi, Sc, Ba (3–5), Cu, Co, and Ni (1.5–3) accumulate in the technogenic silts of the creek. Active sedimentation determines the lithological diversity of the channel, when areas composed of either typical sandy alluvium or technogenic silts alternate within its limits; fluffly layers are common on point bars. The lithological diversity of sediments largely determines the spatial inhomogeneity of the chemical element distribution in

Table 50. Chemical element distribution in Pakhra technogenic silts in zone of influence of Podolsk

Element	Areas									
	1		2		3		4		5	
	K_C	%*	K_C	%	K_C	%	K_C	%	K_C	%
Ag	8.4	84	29.2	203	13.8	199	138.2	98	256.3	73
Hg	6.9	206	10.9	169	76	510	28.9	91	57.5	66
Cu	2	67	2.9	126	2.6	224	10.9	66	19	59
Co	1.8	33	2.2	18	1.7	48	1.9	33	1.7	35
Sr	1.7	28	1.5	22	1.8	62	1.9	39	1.9	52
Pb	1.7	99	4.3	160	2.7	136	11.9	15	21.7	74
Sn	1.4	53	2.6	146	3	140	7.1	84	17.9	103
Ni	1.2	47	2.5	109	1.8	96	7.8	67	49.2	87
Zn	1.1	66	2	100	1.8	130	4.6	57	5.2	64
V	1	54	1.5	51	1	54	1	40	1.4	31
Mo	1	61	0.4	60	0.9	46	1.7	175	1.4	70
Cr	1	43	2	96	0.8	62	3.2	67	9.7	85
Cd	–	–	–	–	–	–	27.5	106	785	125

Element	Areas				On average for all areas	
	6		7			
	K_C	%	K_C	%	K_C	%
Ag	113	93	26.5	149	76	144
Hg	21.6	116	3.4	298	34	569
Cu	8.3	61	5.3	209	7	117
Co	1.9	20	1.6	34	1.8	34
Sr	1.5	28	1.1	22	1.7	47
Pb	5.7	114	1.5	129	6.2	125
Sn	43.3	302	5	144	17	466
Ni	15.3	102	2.4	68	7.5	177
Zn	2.6	77	1.9	154	2	96
V	1	46	0.7	66	1	52
Mo	1	28	0.8	50	1.1	148
Cr	6.3	181	1.2	62	3	195
Cd	110.7	180	12.2	179	55	384

* Variation coefficient, %.

river sediments. In some points of the channel, some of them have very high concentrations: Hg (K_C up to 2200), Ag (up to 150), and Sn (up to 20). As a rule, the most intensively accumulating elements demonstrate a well-pronounced spatial correlation for their concentration distribution. The extent of the established technogenic anomalies is quite large (up to 3–4 km), although at the end of this area, the contents of many pollutants in channel sediments are significantly lower.

Within area 4, starting from the mouth of Cherny Creek, which is Podolsk's main wastewater channel, technogenic silts actively participate in the composition of the riverbed. A certain amount of wastewater is discharged into the Pakhra through to the system of streams flowing into it from the left bank, in the beds of which silts are also widespread. In essence, this segment of the Pakhra's channel is the main technogenic pollution zone, within which high concentrations of many chemical elements and compounds thereof are stably observed in river waters (Yanin, 2003b). There is a sharp increase in the content of a wide group of chemical elements in silts (both in streams and in the Pakhra). The heaviest and most extensive anomalies are recorded for Ag (K_C = 400–500); Hg and Cd (up to

Table 51. Correlation matrix of chemical element content in bottom sediments of area 2

	Hg	Mo	Pb	Zn	Ag	Cu	Co	Ni	V	Cr
Sr	0.46	−0.63	0.40	0.46	0.19	0.33	−0.32	0.12	−0.28	0.13
Cr	**0.92**	−0.66	**0.89**	**0.89**	**0.99**	**0.97**	−0.17	**1.0**	***−0.85***	
V	−0.73	0.43	−0.76	−0.70	***−0.89***	***−0.82***	0.36	−0.85		
Ni	**0.91**	−0.66	**0.93**	**0.89**	**0.99**	**1.0**	−0.17			
Co	−0.30	0.32	−0.31	−0.30	−0.22	−0.28				
Cu	**0.98**	***−0.81***	**0.99**	**0.97**	**0.98**					
Ag	**0.92**	−0.66	**0.94**	**0.90**						
Zn	**1.0**	***−0.93***	**0.99**							
Pb	**1.0**	***−0.88***								
Mo	***−0.90***									

Confidence intervals of coefficients
correlations with the significance level
5% = **0.81**; 1% = 0.92; 0.1% = 0.97

100–150); and Pb, Ni, Sn, Cu, and In (up to 20–40). In constrast to previous areas, where the element contents in sediments even at neighboring sampling sites ranged from highly abnormal to background, here the technogenic anomalies are spatially stable. For example, the K_C value of cadmium varies at neighboring sampling sites from 15–20 to 30–50 (sometimes up to 100); Ag, from 70 to 300–500; Sn, from 5–10 to 15–20; Hg, from 10–15 to 40–50 (sometimes up to 70–100). In general, the elements included in the geochemical association are characterized by a uniform spatial distribution of concentrations and a very high degree of correlation (Table 52). The inhomogeneity of the distribution increases only in the lower part of the area, which may be due to the lithological–geomorphological structure of the channel (including sharp bends in its longitudinal profile). Thus, the presence of a powerful source of technogenic sediment supply led to the formation of technogenic silts in the Pakhra's channel, which are distinguished by high concentrations of a wide group of chemical elements, relative stability of the spatial distribution of the latter, and their high degree of correlation.

The river sediments within the next area 5 (immediately before the Shcherbinsky landfill), slightly more than 1 km in extent, is characterized by high average concentrations of Cd (K_C = 786), Ag (265), Hg (68), Ni (63), Pb (22), Cu (19), Sn (18), Cr (10) and elevated levels of certain other elements. As a rule, the concentration levels of many elements here are higher than in sediments in the previous area of the river, which is mainly due to the geomorphological structure of the Pakhra River channel, which contributes to the accumulation of sediment transported by the river and more intensive precipitation of dissolved matter (sharp flattening of the longitudinal channel profile, the presence of islands and troughs, intensive development of aquatic vegetation in the latter, and appreciable narrowing of the channel at the confluence with the Konopelka River, which creates a backwater effect). A distinctive feature of this area of the river channel is a discontinuity in the correlations between the spatial distribution of chemical elements in bottom sediments. Undoubtedly, in this area, in addition to mechanical sedimentation, sorption from solution and the formation and subsequent precipitation of colloids play an important role in the removal of pollutants from the migration flow. Thus, geochemical anomalies recorded by river sediments are formed by the action of several sources of pollutants entering them, which obviously disrupts the correlations between chemical elements.

Within area 6 (zone of influence of the Shcherbinsky landfill), the highest chemical element concentrations are naturally confined to the mouth of the Konopelka River. Directly below the landfill, the plots of the element distribution in silts still sharply vary and all elements show a tendency toward a decrease in content. The spatial distribution of most chemical elements is characterized by a positive correlation. The influence of the Rozhaya River (area 7), which receives runoff from Domodedovo, is recorded as a slight increase in the Ag, Ni, Cd, Zn, Hg, and Sn contents in river sediments. Below the Rozhaya River, already in Pakhra River sediments, increased and slightly varying concentrations of almost all of these metals can be decreasingly traced for about 3 km. Exceptions are Ag, Sn and Cu, the contents of which still significantly exceed the background. The spatial correlation between chemical elements within the studied area is generally weakly pronounced.

Thus, the technogenic pollution zone recorded by the accumulation levels of chemical elements in channel sediments extends for more than 40 km. In its structure, several specific areas are distinguished, characterized by peculiarities in the concentration and spatial distribution of elements in sediments unique only to them, which is determined by the uniqueness of pollution sources and geomorphological structure of the river channel and valley. In general, the Pakhra is characterized by a significant level of technogenic

Table 52. Correlation matrix of chemical element contens in bottom sediments of area 4

	Hg	Sn	Pb	Cd	Zn	Ag	Cu	Co	Ni	V	Cr
Sr	**0.54**	**0.72**	**0.81**	**0.78**	**0.80**	**0.82**	**0.80**	**0.50**	**0.88**	0.35	**0.81**
Cr	**0.63**	**0.87**	**0.85**	**0.90**	**0.85**	**0.95**	**0.87**	**0.55**	**0.91**	**0.53**	
V	0.33	**0.36**	**0.48**	**0.40**	**0.49**	0.44	0.42	**0.52**	0.41		
Ni	**0.65**	**0.85**	**0.85**	**0.90**	**0.88**	**0.92**	**0.91**	**0.51**			
Co	**0.59**	**0.45**	**0.58**	0.41	**0.72**	0.44	**0.50**				
Cu	**0.74**	**0.91**	**0.87**	**0.93**	**0.87**	**0.90**					
Ag	**0.62**	**0.88**	**0.84**	**0.93**	**0.83**						
Zn	**0.70**	**0.76**	**0.79**	**0.80**							
Cd	**0.70**	**0.96**	**0.89**								
Pb	**0.70**	**0.88**									
Sn	**0.69**										

Confidence intervals of correlation coefficients with significance level of 5% = 0.35; 1% = **0.45**; 0.1% = 0.56

Table 53. Assessment of state of Pakhra River in zone of influence of Podolsk

River area	Z_C	Z_{ST}	Pollution level	Degree of sanitary–toxicological hazard
1	18	17	Average	Moderate
2	52	46	High	Hazardous
3	98	94	High	Hazardous
4	234	211	Very high	Very hazardous
5	1216	1135	Extremely high	Extremely hazardous
6	315	290	Extremely high	Very hazardous
7	52	46	High	Hazardous
Total	200	185	Very high	Very hazardous

pollution and a high degree of sanitary–toxicological hazard (Table 53).

In the literature, technogenic flows of chemical elements in river sediments are usually considered linear objects spreading downriver from pollution sources. In fact, they have not only a linear extent, but also a width and vertical thickness. At one time, this was shown for ore-related dispersed flows (Polikarpochkin, 1976). Knowledge of the spatial distribution of pollutants both over the channel area and silt sequence is of methodological and practical importance, since it allows one to detail the processes involved in formation of pollution zones in river channels, to assess the real pollution level of rivers and individual areas thereof, etc. For these purposes, on the Pakhra River, a study was made of the areal distribution of chemical elements in the river channel in an area (with a total length of 0.5 km) that is a wastewater–river water mixing zone (the mouth of Cherny Creek and the adjacent channel of the Pakhra River). Figure 14 shows the lithologic scheme of this area, and Fig. 37, as a typical example, shows a scheme of the areal distribution of copper in the upper (0–20 cm) layer of channel sediments. This area of the channel is distinguished by lithologically diverse sediments, especially near the mouth of Cherny Creek, as well as a dynamic water regime and the presence of zones of jet currents, confined mainly to the left bank of the Pakhra. In general, the river–wastewater mixing zone is characterized by conditions hardly favorable for material to accumulate; here, the channel restructuring processes are rather intensely manifested mainly due to migration of the channel microrelief. In many respects, these phenomena are controlled by the position of the area's boundaries in the influx zone of powerful water runoff from Cherny Creek into the Pakhra River. The heaviest sedimentation is confined to island bars, as well as to the right bank of the Pakhra, which has a shallower and calmer flow regime. The downstream part of the studied area is characterized by an already established flow regime, which is reflected here in a virtually continuous zone of technogenic silts that almost completely covers the riverbed (the vertical thickness of silts is 30–50 cm).

Immediately below the mouth of Cherny Creek, the highest copper contents (as well as the contents of many other chemical elements) are confined to sandbars and the right bank of the river. Relatively low element concentrations are observed in coarse-grained river sediments corresponding to the zone of the most significant flow. The lower part of the studied area, which is recorded in the occurrence of sandy-silty and

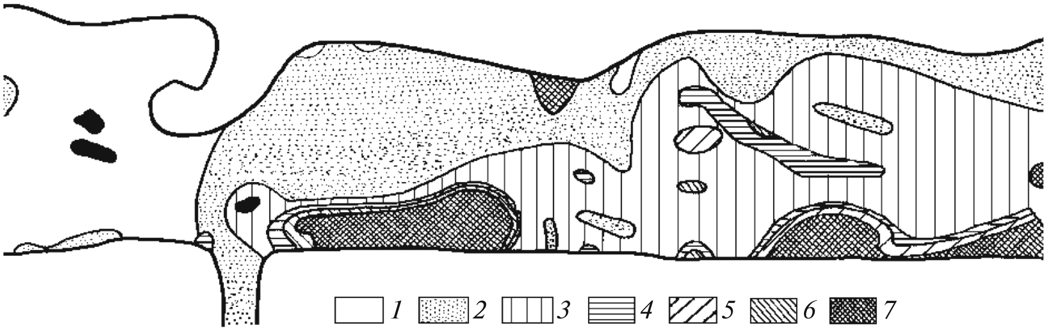

Fig. 37. Copper in bottom sediments of Pakhra River in wastewater—river water mixing zone—copper concentration coefficients: (*1*) less than 1.5; (*2*) 1.5–3; (*3*) 3–6; (*4*) 6–9; (*5*) 9–12; (*6*) 12–15; (*7*) more than 15; islands are shown in black.

silty sediments, is characterized by widespread sediments with high and very high chemical element concentrations (Hg, Ag, Cd, Sn, Pb, Cu, etc.). In the general case, there are significant excess levels of elements in river sediments below the mouth of the creek compared to areas above it. The formation of geochemical anomalies within this area is mainly due to hydraulic sedimentation of SPM transported with wastewater. The heaviest sedimentation zones are confined to areas of decelerated flow, manifested in the accumulation of sandy-silty and silty sediments, which in turn are characterized by higher chemical element concentrations. Thus, even in the complex and dynamic conditions of the wastewater—river water mixing zone, active settling of pollutant-enriched sedimentary material occurs, along with the formation of stable pollution zones.

The channel morphology of lowland watercourses used in technogenic landscapes as wastewater collectors is an important factor in the localization of technogenic silts. From this aspect, the nature of the longitudinal profile and structure of the mouth zones of watercourses are particularly important. Small watercourses usually have high slopes. When next-order flows enter the river (with a well-developed floodplain), their longitudinal profile flattens out dramatically, which causes the formation of geochemical (primarily mechanical) barriers and accumulation of silts in the mouths of watercourses, which concentrate heavy metals.

The studied situation in the zone of influence of Troitsk is a typical example of common coupling: the source of pollution (a city whose wastewater flows into city treatment plants) is a stream that receives wastewater from treatment plants—a small river into which the stream flows (Yanin, 2004a). In this case, wastewater after treatment at the plant was discharged into Oranka Creek (which flows into the Pakhra River). More than 90% of the stream's water runoff was formed by effluents. The valley of the stream has an oval shape, which sharply narrows toward the mouth, its sides are high and steep, the bottom is flat, up to 5—20 m wide, and the meandering channel cuts into it by 0.3—0.5 m. The longitudinal profile of the midstream has a significant slope; when it enters the Pakhra floodplain, it flattens out dramatically. The widespread sediments in the stream are mainly technogenic silts. Their especially heavy accumulation was observed at the mouth of the stream and the adjacent part of the Pakhra's channel, where an alluvial fan formed (vertical thickness of silt, 1 m or more). An important feature of the chemical element distribution in silts of the Oranka Creek is their spatial inhomogeneity, which is reflected in the high variation coefficients calculated for the entire observed pollution zone (Table 54). A certain zoning is observed in the metal concentration intensity and the character of spatial changes in their contents in silts in the structure of the established pollution zone: in this case, the existence of channel areas with a specific element distribution in sediments. The revealed zoning is the result of peculiarities in the geomorphological structure of the stream channel (particularly the nature of its longitudinal profile) and the presence of a river—wastewater mixing zone. Thus, in silts of the upper and middle parts of the stream (which differ by the significant slope of the longitudinal profile), a nonuniform distribution of the majority of studied metals is observed. When the stream enters the Pakhra's high floodplain, its longitudinal profile sharply flattens, which causes the formation of a lateral geochemical (mechanical, sedimentation) barrier and favorable accumulation conditions (hydraulic deposition) for sediment transported by the stream (Table 54, Fig. 38). Metal sorption and coprecipitation processes obviously play a certain role. All this leads to chemical element accumulation in sediments within the geochemical barrier. The exception is Pb, which hardly accumulates at all at the barrier. As a rule, metals characterized by high K_C values before the barrier concentrate more intensely within it.

In the metal distribution in silts, the Oranka shows a high correlation (Table 55). This indicates that metals are transported by runoff (mainly with SPM) and migrate synchronously in the watercourse, which results from a single source (city wastewater treatment

Table 54. Distribution of metals in technogenic silts in zone of influence of Troitsk

Metal	Average K_C value	Variation coefficient, %	Intensity of metal accumulation in silts at the geochemical barrier			
			K_C before barrier	K_C at barrier	K_C after barrier	barrier intensity
Ag	91	204	140	600	25	4.3
Cd	17	328	18	188	1.1	10.4
Hg	7	268	6	58	1.3	9.7
Cu	3.1	112	5.4	13	1.1	35.4
Zn	2.7	126	5	13	2	2.6
Bi	2.2	214	3.5	4	1.5	1.1
Pb	2.2	171	3.1	11	2	3.6
Sn	2	125	2.5	7	1.2	2.6
Z_C	120	–	178*	890**	28***	5

* Very high level of industrial pollution; ** extremely high pollution level; *** average pollution level.

plants) and the generality of their mode of entry into the stream. The exception is Pb, for which no correlation can be traced for some elements. Obviously, it is transported not only by runoff (mostly in dissolved form, apparently), but also as part of surface runoff from the catchment area.

The presence of a geochemical barrier determines the formation of zones with extremely high pollution levels. Whereas before the barrier, the Z_C values correspond to a "very high pollution level," an "extremely high pollution level" is already recorded within the barrier, while after the barrier, the pollution intensity decreases sharply (to the "average pollution level").

Thus, in small streams, the intensity of lateral migration and, accordingly, the spatial chemical element distribution in bottom sediments in the zone of influence of pollution sources are largely governed by the geomorphological structure of the channel and, above all, the character of their longitudinal profile and morphology of the mouth zone, which determines the possibility of pollutants passing into a next-order river.

Mordovia region. The chemical element content in background channel alluvium of the Insar River is close to the concentrations in background soils; it also correlates well with the levels of its global distribution known in the literature (Yanin, 2002c, 2011). The observed deviations from the global distribution parameters (higher B and Co contents in soils, slightly lower Sc, Ti, Fe, and Zr concentrations in soils and alluvium, and Fe, Zn, and Ga in alluvium) can be explained by the features of the parent rocks and formation conditions of the lithogenic facies of channel alluvium (Table 56).

Technogenic silts widely encoutered in the Insar's channel and its main tributaries within and below Saransk are characterized by very high concentrations of many chemical elements, exceeding their background levels by many times (Yanin, 2002c, 2007c).

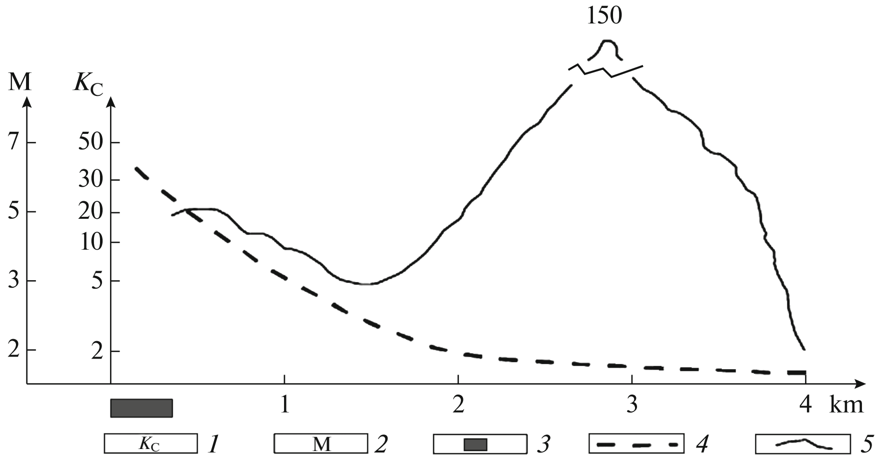

Fig. 38. Cadmium in Oranka Creek bottom sediments: (*1*) cadmium concentration coefficient; (*2*) excess above waterline of mouth of creek, m; (*3*) city; (*4*) line of longitudinal profile of creek; (*5*) cadmium concentration distribution.

Table 55. Correlation matrix of chemical element distribution in technogenic silts

	Sr	Cu	Ag	Zn	Cd	Pb	Bi	Sn
Hg	**0.57**	**0.84**	**0.83**	**0.79**	**0.83**	0.12	**0.80**	**0.75**
Sn	**0.65**	**0.85**	**0.84**	**0.89**	**0.58**	0.30	**0.75**	
Bi	**0.74**	**0.84**	**0.88**	**0.67**	**0.77**	0.30		
Pb	**0.54**	**0.41**	0.35	**0.50**	0.10			
Cd	**0.40**	**0.61**	**0.61**	**0.63**				
Zn	**0.65**	**0.76**	**0.77**					
Ag	**0.81**	**0.96**						
Cu	**0.76**							

Confidence intervals
of correlation coefficients for significance
levels: 5% = 0.31; 1% = 0.39; **0.1% = 0.49**

Heavy metals are expecially concentrated in them. In the general case, associations characteristic of industrial silts in river areas directly below the city are very close in quality (set of chemical elements) and quantitative (relative position of these elements in the series of concentration coefficients K_C) parameters to the associations established for SS and wastewater SPM (Table 57). The element distribution in silts widespread in the channel within the city is characterized by spatial inhomogeneity typical of pollution zones (Fig. 39). With distance from the city, the element concentration in silts decreases, the variability of distribution decreases, and the quantitative relationships between the elements change (their position in the association changes). All these changes result from secondary transformation and redeposition of sediments, including blending of technogenic substances with natural sedimentary material.

Naturally, the qualitative composition of geochemical associations and the concentration intensity of some elements are influenced by the technogenic flow that forms in the southern and, especially, in the central industrial zone of Saransk as a result of water runoff entering the Insar via the Lepeleyka River and Nikitinsky Creek (areas I–IV). Nevertheless, the main metals in SS and WSPM —Cd, Sn, Ag, Mo, Hg, and Zn—retain their leading position in the geochemical association of silts. It is these elements that, in fact, determine the ecological and geochemical characteristics and the level and degree of sanitary–toxicological hazard of technogenic pollution. Virtually throughout the entire length of the Insar, technogenic silts in total mass are characterized by a high total pollution indicator (Fig. 40).

The existing stratification of silts, especially in maximum accumulation areas, is reflected in the peculiar inhomogeneous vertical distribution in their chemical element sequence (Fig. 41). The recorded stepwise-decreasing character of the distribution of pollutants with a regular decrease in concentration in silt layers in contact with base of the channel results from the processes of their secondary redistribution and entry into silt, bottom, and subriverbed water. In most cases, the maximum content of chemical elements is confined to the upper silt layer, which a priori determines their significance as secondary pollution sources of the water mass. It is also indicative that the uppermost silt layer is usually depleted in lithophile elements, which points to the leading role freshly deposited technogenic material in its formation.

Thus, the existing stratification of silts and the unique chemical element accumulation in them are reflected in the peculiar vertical distribution of the latter in the sediment sequence. Apparently, active physicochemical microzones, differing in their geochemical impact, form in the silts. Thus, the 40–60 and 120–180 cm layers are clearly distinguished by active processes that facilitate metal migration both in higher and lower levels of silts. A similar element distribution is observed (with a certain displacement of the boundaries) in other parts of the channel where two layers with the maximum accumulation of the most heavily concentrated chemical elements, 0–60 and 120–180 cm layers, are clearly distinguished. One should also note the marked trend of increasing Z_C values calculated for lithophile elements from upper to lower technogenic silt horizons, especially when comparing the element concentration levels in the 0–120 and 120–300 cm layers. This may be due to more substantial reworking of the lower strata of technogenic silts by diagenetic processes (mineralization of organic matter; dilution with channel alluvium; vertical and lateral, including filtration, flow; element migration; etc.), which result in the transition of chemical elements to the uppermost river sediment horizons and, partly, into subriverbed waters.

Kazakhstan region. Analysis of the geomorphological features of the Nura River channel in the area from Temirtau (from the dam of the Samarkand reservoir) to the village of Samarka, the nature of the mercury distribution in technogenic silts, and the distribution of the latter over the channel area makes it possible to identify a number of characteristic areas in the structure of the recorded technogenic sedimentation zone: I, the channel from the dam of the Samarkand reservoir to the mouth of the main wastewater channel (MWC); II, MWC; III, from the mouth of MWC to the village of Gagarinskoe; IV, from Gagarinskoe to

Table 56. Chemical elements in background soils and background alluvium, mg/kg

Element	Background soils Insar basin						Alluvium, Insar	Average in lithosphere (Vinogradov, 1962)
	catchment area		slope		terrace			
	1*	2**	1	2	1	2		
Li	25	25	25	25	25	25	28	32
Be	–	–	–	–	–	–	1.1	3.8
B	54	55	63	74	65	60	32	12
F	–	–	–	–	–	–	350	660
Sc	2.1	1.7	2.5	2.2	2.3	2.9	4	10
Ti	3360	4130	4710	4960	3240	4770	3600	4500
V	80	110	95	130	100	140	85	90
Cr	49	77	67	96	51	70	62	83
Mn	1200	680	1150	500	1050	700	770	1000
Co	21	16	24	20	15	18	9	18
Ni	26	38	25	38	26	35	35	58
Cu	50	45	54	55	52	44	41	47
Zn	85	110	95	95	100	110	50	83
Ga	21	27	24	29	24	26	11	19
Ge	–	–	–	–	–	–	0.9	1.4
As	6.4	–	–	–	–	–	7	1.7
Sr	28	35	30	35	45	50	45	340
Y	11	7	12	6	10	9	10	29
Zr	75	95	125	90	125	105	86	170
Nb	–	–	–	–	–	–	6	20
Mo	0.7	1.1	0.9	1.3	0.9	1.2	2	1.1
Ag	0.05	0.05	0.04	–	0.06	–	0.08	0.07
Cd	0.34	–	–	–	0.33	–	0.14	0.13
Sn	2.4	3.2	1.9	3.5	1.9	3.4	2	2.5
Sb	1	–	–	1.1	1	–	0.9	0.5
Ba	210	110	220	150	220	150	210	650
Yb	1	0.9	1.1	1	0.8	0.9	1	3.3
W	1.5	1.5	1.4	–	1.6	–	1.3	1.3
Hg	0.06	–	0.05	–	0.05	–	0.02	0.083
Tl	0.19	–	–	–	0.21	–	0.13	1
Pb	15	11	18	18	13	11	17	16
Number of samples	25	24	25	24	25	22	50	–

* Horizon A (usually 0–10 cm), ** average for horizons B_1–B_3.

the village of Rostovka; V, from Rostovka to the Intumak reservoir; VI, Intumak reservoir zone; VII, from the Intumak reservoir to the Samara reservoir; VIII, below Samarka (Fig. 42). On the whole, this segment of the Nura is characterized by intense technogenic mercury anomalies in silts, which are stable in length, channel area, and sediment sequences themselves (Yanin, 1989, 1992).

Area I is characterized by silt accumulation zones of significant area, the maximum thickness of which reaches 1.2 m. A characteristic feature of the channel in this area is a markedly diverse lithological composition of its sediment cover. There is an alternating sand and gravel-pebble, variously grained and silty sands, and technogenic silt. This is due to the unstable hydrodynamic regime of the watercourse, due to the periodic discharge of water from the reservoir and surface runoff from the urban area. Water inflow from the reservoir and especially surface runoff (rain and meltwater) are the main reason for the technogenic mercury

Table 57. Geochemical associations in technogenic silts (I–XII), sewage sludge (SS), and wastewater SPM (WSPM)

Area*	K_C values of chemical elements					Z_C	Z_{ST}
	>100	100–30	30–10	10–3	3–1.5		
Above city	–	–	–	Bi	Pb–Zn–Sn–P–Cu–Cr–W–Ga–Hg	12	8
I	Sn	Bi	Cu–Ni	Zn–Ag–Cr–Pb–W	Tl–Sr–Hg–Ga–P	275	106
II	–	–	Hg	Bi–Pb–Zn–Sn–Sr–Ag–Cu	W–B–Ga	56	40
III	Cd–Hg–Mo	Zn	Sn–Cu–W	Ag–Ni–Pb–Cr–Sr	F–Tl–V–Ga	810	705
IV	Cd	Hg–Sn	Cu–Mo	W–Ag–Zn–Bi–Ni	Cr–Pb–Sr–PB–Ga–Tl–F	210	185
V	Sn	Cd	Hg–Mo–Bi	Cu–Ag–Zn–Cr–Pb–W	Li–Tl–Ni–P–Sr–Co–Be	358	175
VI	Sn	Cd–Hg	Mo–Be–Cu	Zn–W–Ag–Pb–Ni–Cr–Bi	Sr–Tl–B–F–Li–Co	318	170
VII	Sn	Cd	Mo	Zn–Cu–Tl–Ag–Pb–Cr–Hg	W–Bi–B–Ni–Sr–Ga–PF	220	95
VIII	–	Cd–Sn	Cu	Zn–Hg–Mo–Ag–Tl–Cr	W–Ni–Pb–Bi–Sr–Co–Li	186	100
IX	–	–	Sn	Mo–Cu–Tl–Cd–Zn	Sr–Ag–Pb–Bi–Cr–Hg–Ga	31	19
X	–	–	–	Sn–Cd–Tl–Cu–Zn	Ag–Hg–Mo–Pb–Sr–Cr–Ga–Bi	23	14
XI	–	–	–	Sn–Mo–Cu	W–Sr–Sn–Tl–Cr–Cd–Hg	19	12
XII	–	–	–	Mo	Zn–V–Pb–Co–Tl–Ni–Ag–Sn–Cu–Ga–Hg	16	10
SS	Cd–Sn–Hg	Ag–Zn–Bi–W–Cu–Cr	Mo–Ni–Sb	F–Be	Sr–Tl–U	1140	760
WS	Cd–Mo–Sn	Ag–Zn–Hg–Bi	Cu–W	Ni–Cr–P–Pb–Sb	As–Sr–Be–F	1020	700

* Hereinafter, location of areas I–VIII is shown in Fig. 24; areas IX–XI, respectively, are 49, 62 and 92 km (mouth of Insar) below area I; area XII, Alatyr River (70 km below mouth of Insar).

anomalies, the concentration of which in silts is on average 170 times higher than the background (Table 58).

The relatively high mercury concentrations in channel sands seem noteworthy, which is apparently due to its sorption in large fractions and the presence of silt filler in sandy sediments. The existing lithological diversity of channel-forming sediments results in very high variability in the mercury distribution over the area of the channel (the variation coefficient is about 330%).

The MWC is virtually filled with technogenic silts throughout its extent. Their vertical thickness in its lower part, even despite the strong current, reaches 1.8 m. The mercury levels in more than 50% of samples are extremely high (100–600 mg/kg), exceeding the background by a factor of 1000 (Table 59). As a rule, the upper layers (up to 20–30 cm) of silts are consistently characterized by mercury concentrations of 100–200 mg/kg throughout the channel, reaching 300–600 mg/kg. Lower levels (7–40 mg/kg) are more frequently found in the 30–60 cm layer, and downsection, mercury concentrations, rather sharply and irregularly varying, increase to 300–600 mg/kg. Obviously, the mercury concentration in the lower silt layers is sharper because they formed when mercury was discharged into the watercourse in the 1960s–1970s.

Area III (length ~10 km) is characterized by the maximum mercury pollution level of the channel (Table 60). At the same time, this is the zone with the heaviest deposition of technogenic silts. Therefore, here, silt covers from 44 (pronounced rolling) to 98% of the channel area (on average, about 78%). Their maximum vertical thickness ranges from 60 to 340 cm (on average, about 184 cm). Average mercury concentrations in silts on different transects vary from 100 to 560 mg/kg ($K_C = 2272–12726$); maximum levels reach 2000–3000 mg/kg (i.e., 0.2–0.3%). The pollution intensity is such that heavy mercury anomalies have been recorded even in sandy sediments. With distance from the main source of pollution, with an overall high level and against a background of irregular variations, there is a tendency toward a certain decrease in mercury concentrations in both silts and sands. If the silt thickness is no more than 40–60 cm, then the spatial

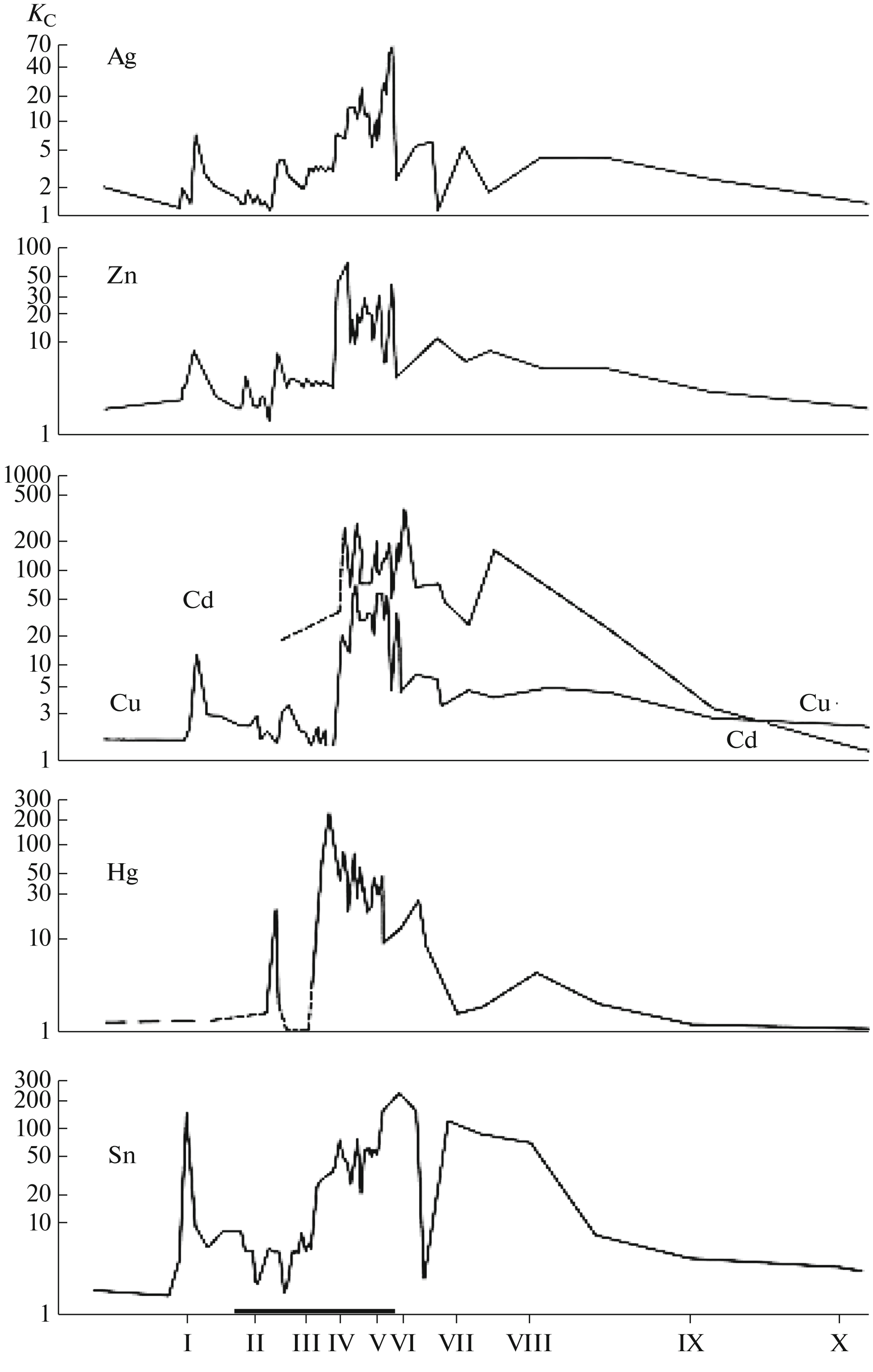

Fig. 39. Distribution of metals in bottom sediments of Insar River in zone of influence of Saransk: K_C, concentration coefficient; I–X, main sampling areas.

distribution of mercury in their sequence is fairly uniform. With greater thickness (>1–1.5 m), its vertical distribution can vary. Thus, maximum levels (up to 1000–2000 mg/kg) have been very frequently noted in the 60–90 cm layer. In other cases, there may be a gradual decrease in mercury concentrations from the 0–50 cm layer downward, or vice versa, a sharp increase in lower silt horizons. Apparently, the inhomogeneity of the vertical (as well as areal) mercury distribution in the silt sequence reflects the rather complex process of their accumulation in the river channel (redeposition, diagenetic processes, etc.). In terms of potential impact of silts on the aqueous phase, the significant, nearly ubiquitous enrichment

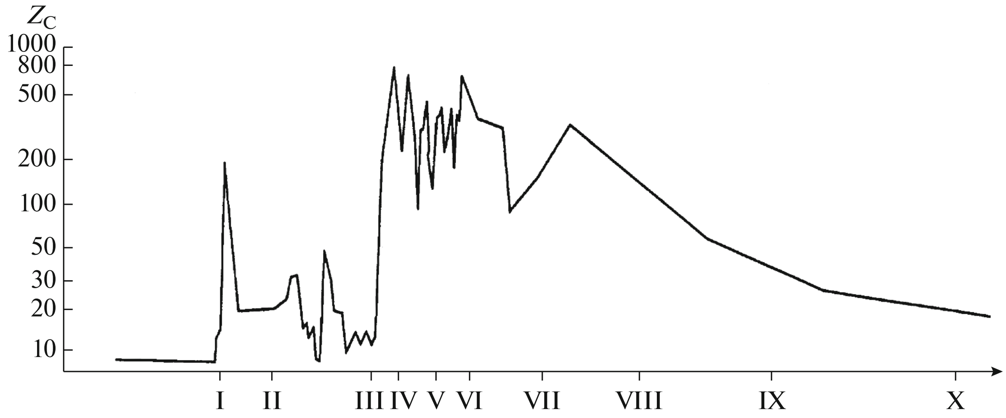

Fig. 40. Distribution of total pollution index Z_C in Insar River sediments in zone of influence of Saransk; I–X, main sampling areas.

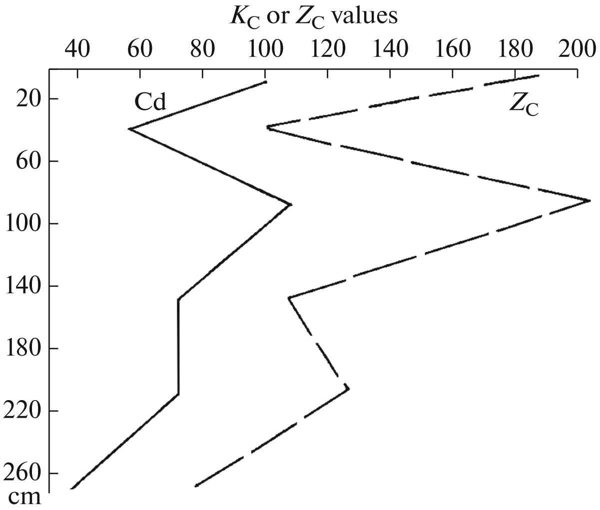

Fig. 41. Distribution of K_C values of cadmium and Z_C in technogenic silt sequence of Insar River, area V.

of their upper, most active part in mercury is particularly hazardous: it can involve not only the release of its dissolved forms (from silt water) into the water column during various physicochemical alterations, but also transport of the metal with sediments as the water flow mechanically acts on the underlying deposits. Mercury reserves in sediments in this area of the river are estimated at about 84.3 t, with the overwhelming majority bound with silts.

In the general structure of channel-forming sediments in area IV (from Gagarinskoe to Rostovka), silts occupy a significantly smaller share than in the previous area (Table 61). Nevertheless, even 20–30 km from the main source of pollution, very high levels of this metal (up to 100–200 mg/kg) have been recorded in bottom sediments.

It is in this area of Nura that rather large backwaters are commonly found, filled with a thick (up to 1.5 m) silt sequence in which mercury concentrations frequently reached 100 mg/kg, especially in the upper 50 cm. The significant (in some cases, predominant) participation of typical river sands (although also silt) in the channel structure (and its pronounced lithological diversity) contribute to the sharp increase in areal inhomogeneity of the mercury distribution. Vertical inhomogeneity is even more pronounced when, even within one transect, at virtually adjacent sampling sites, a fundamentally different mercury distribution in the silt sequence is observed (Fig. 43). Hg reserves in sediments in this segment of the river are estimated at almost 43 t.

Table 58. Mercury and technogenic silts in Nura River channel in area above main wastewater channel*

Indicator	Technogenic silts	Sands	Deposits as a whole
Mercury, mg/kg, average (limits)	7.5 (0.5–100)	1.0 (0.3–4)	6.8 (0.3–100)
K_C, medium (limits)	170 (11–2273)	23 (7–91)	155 (7–2273)
Share of sediments from area of channel in transect, %	48	52	100
Maximum sediment thickness, cm	120	–	–
Amount of mercury, t**	0.54	0.15	0.69

* Background mercury content in typical channel alluvium of Nura River (upper reaches), 0.044 mg/kg; ** hereinafter for silts, taking into account their entire mass; for sands, in the upper (0–20 cm) layer.

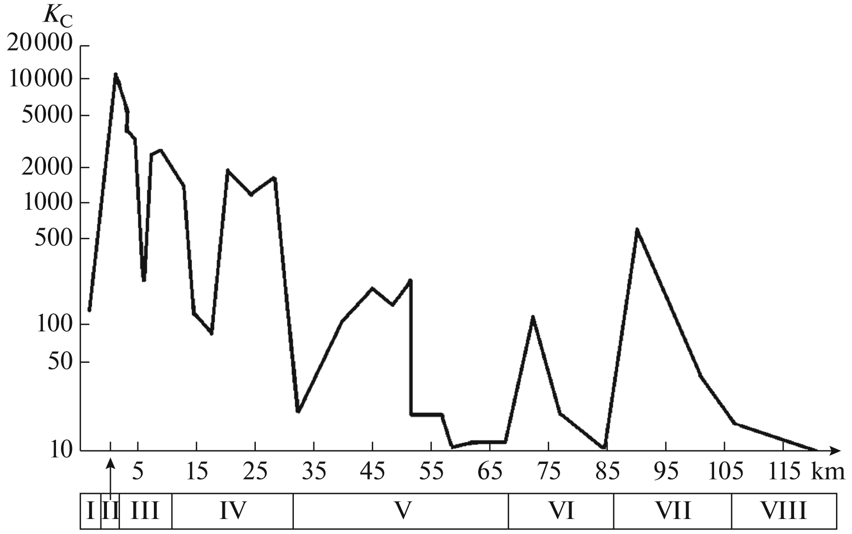

Fig. 42. Mercury in channel deposits of Nura River: K_C, concentration coefficient; I–VIII, highlighted areas.

Area V (from Rostovka to the upper reaches of the Intumak reservoir) is divided into three zones according to mercury content levels based on the characteristics of the channel process within each one. The boundaries of the zones are well distinguished according to the averaged data on the distribution of mercury and technogenic silts over the channel. At the beginning of this area, the silts make up a substantial part of the channel (Table 62), distinguished by intense mercury anomalies (tens and hundreds of times higher than the background). The next zone (transects 23–28) is characterized by a clear predominance of channel erosion processes, which contributes to the dilution and removal of technogenic matter and, accordingly, “decreases” technogenic anomalies. The mercury concentration coefficients average 16–25, and they can even be somewhat higher in sands than in silts. This is due to the presence of silts in sandy sediments. This, in turn, points to the active erosion of technogenic silts and their secondary redeposition (dispersion) along the entire river channel in the con-

Table 59. Mercury and technogenic silts in main wastewater channel

Indicator	Value
Mercury mg/kg, average (limits)	103 (7–600)
K_C, medium (limits)	2341 (159–13636)
Maximum thickness of silts, cm	180
Amount of mercury, t*	1.18

* For average silt thickness of 50 cm.

Table 60. Mercury and technogenic silts in channel of Nura River in Area III

Transect (distance from MWC, km)	Average mercury content, mg/kg (K_C)				Maximum thickness of silts, cm	Share of silts from channel area, %	Amount of mercury in sediments, t
	technogenic silts	sand	average for all sediments	variation coefficient, %			
2 (0.5)	129 (2932)	7 (159)	100 (2272)	69	60	63	0.65
3 (1.1)	560 (12727)	100 (2272)	550 (12500)	195	200	60	8.1
4 (1.4)	460 (10455)	10 (227)	440 (10000)	86	150	50	4.25
5 (2.6)	293 (6659)	10 (227)	290 (6591)	341	340	96	20.9
6 (2.9)	250 (5682)	10 (227)	240 (5455)	70	140	98	4.9
7 (3.2)	185 (4204)	5 (114)	180 (4091)	44	180	98	2.9
8 (4.4)	164 (3727)	4.3 (98)	140 (3182)	53	200	50	7.05
9 (5.4)	11.1 (252)	2.5 (57)	8.4 (131)	84	145	44	0.18
10 (7.1)	100 (2272)	1 (23)	100 (2772)	74	240	98	20.1
11 (9.0)	127 (2886)	5.3 (120)	97 (2205)	106	180	80	15.25
Average	228 (5182)	15.5 (352)	215 (4886)	112	184	78	84.28

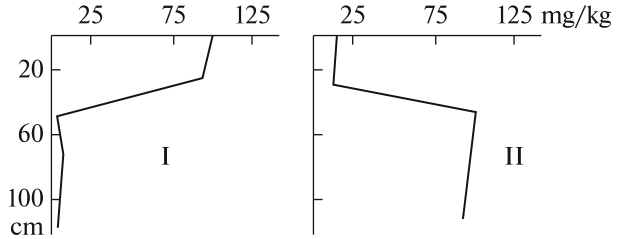

Fig. 43. Vertical distribution of mercury at transect 16 (distance between sampling verticals I and II is 6 m).

sidered area. At the end of this area, the river valley widens significantly, the channel splits into two separate channels, which is reflected in the intensified sediment accumulation (transect 29). This zone is characterized by a wide, swampy floodplain, which from the surface consists of silts with mercury levels 10–25 times higher than the background. Technogenic silts dominate in the structure of sediments covering the river channel, reaching a thickness of up to 50–60 cm. The mercury levels are significantly elevated.

Area VI corresponds to the Intumak reservoir. Its upper part is a complex system of randomly alternating channels, bars, and islands heavily overgrown with vegetation. This creates favorable conditions for the accumulation of silty sediment carried by the river and over a large area as well. Indeed, most of the bars and islands from the surface consist of relatively thin fluffy layers and silty sands, in which elevated concentrations of mercury have been recorded (Table 63). In the lower part of the reservoir, bottom sediments are largely formed due to drawdown of the banks and consist mostly of well washed sands with background mercury levels. However, in thin (up to 3–5 cm) fluffy layers widely encountered on point bars, mercury levels exceed the background by three to times, clearly indicating their technogenic origin. The Intumak reservoir is apparently one of the main "interceptors" of solid material transported by the river. High mercury levels found in clay sediments indicate a significant technogenic load on the given waterbody. This is confirmed by analysis of dry residues of dead planktonic algae from point bars, in which very high (10–14 times higher than the background) mercury levels have been recorded, which indicates the active biological absorption of this metal by planktonic organisms and does not exclude the likelihood of methylation processes, while posing a threat of mercury accumulation in the reservoir's food chain.

The features of the mercury distribution in river bottom sediments within area VII (from the Intumak reservoir to Samarka) clearly indicate the extent of pollution of the Nura River (Table 64). This segment of the river has a very complex geomorphological structure and is characterized by bends, distributaries, and backwaters, which contributes to the accumulation of sedimentary material. Here, areas of the channel are encountered that consist of more than 90% silts with a mercury content hundreds of times higher than the background. Apparently, this area of the channel is a kind of geomorphological trap for a significant portion of mercury-enriched material transported by the river. It should be expected that, downstream, the contrastiveness of anomalies will markedly decrease and sand deposits predominate in the sediment structure. Indeed, below Samarka, the Nura's channel largely consists of sandy and sand–gravel–pebble sediments with mercury concentrations within or slightly differing from the background levels. Only on point bars is there a thin fluffy layer in which weak mercury anomalies are recorded.

Technogenic silts are also widespread in oxbows, backwaters, on islands, and point bars in the Nura River. According to the results of studies in 1997–1998, about 4 t of mercury has accumulated in them (in the area of a valley about 70 km long below Temirtau) (Heaven et al., 2000a, 2000b). A significant area of the Nura floodplain is characterized by very high mercury concentrations in soils and crops, which is released during river floods and floods, and especially

Table 61. Mercury and technogenic silts in channel of Nura River in are IV

Transect (distance from MWC, km)	Average mercury content, mg/kg (K_C)				Maximum thickness of silts, cm	Share of silts from channel area, %	Amount of mercury in sediments, t
	technogenic silts	sand	average for all sediments	variation coefficient, %			
12 (12.5)	65 (1477)	1 (23)	62 (1409)	129	240	71	21.3
13 (14.5)	6.1 (133)	0.5 (12)	3 (68)	298	60	32	0.14
14 (17.6)	4.1 (93)	0.5 (12)	1.7 (39)	216	20	15	0.1
15 (20.6)	100 (2272)	0.8 (18)	46 (1045)	106	120	64	13.6
16 (23.8)	54 (1227)	15 (341)	50 (1136)	87	120	26	4.6
17 (28.8)	82 (1863)	0.46 (11)	41 (932)	314	90	30	3.0
18 (31.9)	1 (23)	0.5 (12)	0.7 (16)	22	40	42	0.1
Average	44.6 (1014)	2.7 (61)	29.2 (664)	167	99	40	42.84

Table 62. Mercury and technogenic silts in Nura River channel in area V

Transect (distance from MWC, km)	Average mercury content, mg/kg (K_C)				Maximum thickness of silts, cm	Share of silts from channel area, %	Amount of mercury in sediments, t
	technogenic silts	sand	average for all sediments	variation coefficient, %			
				Zone I			
19 (39.4)	57 (130)	0.9 (20)	46 (1045)	213	90	59	4.7
20 (44.5)	10.7 (243)	0.4 (9)	7.7 (175)	114	120	34	1.0
21 (48.2)	7.5 (170)	0.48 (11)	5.2 (118)	210	80	27	0.18
22 (51.2)	13.2 (300)	0.61 (14)	6.5 (147)	334	60	74	1.08
Average	21.9 (498)	0.6 (13.6)	16.4 (373)	218	88	49	6.96
				Zone II			
23 (51.5)	1 (23)	0.33 (7.5)	0.95 (21)	15	20	4	0.002
24 (56.6)	1 (23)	0.33 (7.5)	0.58 (13)	7	10	4	0.03
25*	1 (23)	0.37 (8)	0.68 (15)	73	30	25	0.005
26 (58)	0.5 (12)	0.4 (9)	0.41 (9)	8	20	9	0.015
27 (61.5)	0.6 (14)	0.14 (3)	0.34 (8)	88	60	11	0.1
28 (67.5)	0.6 (14)	1.1 (25)	1 (23)	130	40	24	0.15
Average	0.78 (18)	0.55 (12.5)	0.66 (15)	54	30	13	0.27
				Zone III			
29 (72.5)	2.6 (57)	1.6 (36)	2.3 (52)	59	60	56	0.27
				Area V			
Mean	8.7 (198)	0.66 (15)	6.5 (147)	103	54	30	7.38

* Mouth of Sherubaynura River.

Table 63. Mercury in bottom sediments of Intumak reservoir

Sampling site	Characteristics	Average mg/kg (K_C)	Limits, mg/kg (K_C)
Upper reaches	Fluffly layer	1.13 (26)	1–2 (23–26)
	Sands, thin silty	0.66 (15)	0.35–0.90 (8–20)
Bottom part	Fluffy layer	0.32 (7)	0.15–0.40 (3–10)
	Thin sands	0.046 (1)	0.02–0.08 (0.5–2)
	Dry algae*	0.6 (12)	0.5–0.7 (10–14)

* Background mercury content in river macrophytes is 0.05 mg/kg dry weight.

from the use of polluted river water to irrigate floodplain agricultural lands (Yanin, 1992). Technogenic silts are enriched in many other chemical elements: Li, V, Co, Mo, Bi (K_C within 1.5–2, sometimes more), Ba (1.5–3), Cu (2–3), Zn and Sn (2–5), Sr and Pb (5–10), W (10– 15), and As and Ag (3–30). These chemical elements enter the river as part of industrial and domestic wastewater, as well as with surface runoff from developed territories.

Thus, river bottom sediments and, especially, technogenic silts, in which extended (tens of kilometers) multielement geochemical anomalies (technogenic dispersed flows) form, most completely reflect the parameters and morphology of zones of influence of various sources of river pollution. The spatial features of the chemical element distribution in technogenic silts are governed by the geologically insignificant formation time of the latter, the discrete nature of pollutants entering water courses, the channel's natural differentiation of sediments, the lithological–geomorphological structural features of river channels, and the structure and stratification of silts. The most important feature of the chemical element distribution in silts is significant spatial variation in their concentrations both in the sediment sequence and downriver. For most elements, the indicated variation (nonuniform distribution) is usually manifested against their high concentrations. The degree of spatial separation of chemical elements in silts is small and their distribution is usually characterized by a high degree of consis-

Table 64. Mercury and technogenic silts in Nura River channel in area VII

Transect (distance from MWC, km)	Average mercury content, mg/kg (K_C)				Maximum thickness of silts, cm	Share of silts from channel area, %	Amount of Hg in sediments, t
	technogenic silts	sand	average for all sediments	variation coefficient, %			
30 (90.5)	35 (795)	0.4 (9)	34 (727)	51	60	95	9
31 (95.5)	7.9 (180)	0.63 (14)	2.9 (66)	351	30	8	0.16
32 (100.5)	2.5 (57)	1.2 (27)	1.2 (27)	65	20	8	0.1
33 (105.5)	0.8 (18)	0.05 (1.1)	0.47 (11)	115	120	15	0.05
Mean	11.6 (26)	0.57 (13)	9.6 (219)	145	58	31	9.31

tency; a sharp differentiation of geochemical associations is not observed. The natural differentiation and specifics of sediment accumulation in river channels frequently leads to an inhomogeneous (sporadic) areal structure of geochemical anomalies in the bottom sediments of watercourses. Usually, the leading anomalies of the association of a particular pollution source are characterized by more significant anomalies over the channel area. The natural character of the spatial chemical element distribution in channel sediments can be complex at geochemical barriers, the existence of which is due to natural changes in the geomorphological features of the channel and valley (flattening of the longitudinal profile of the watercourse, dramatic expansion of the channel and valley, type of accumulation, etc.), as well as artificial causes (the presence of ponds, dams, etc.). This, on the one hand, contributes to the removal of pollutants from the water flow, and on the other, leads to the formation of zones of increased environmental hazard. Within the technogenic sedimentation zone, areas of the channel are usually distinguished that differ in the overall level of technogenic pollution, the degree of its sanitary–toxicological hazard, and the character of the spatial element distribution. Their formation results from the unique location of pollution sources and peculiarities in the geomorphological structure of the river channel and valley.

FIXATION AND REDISTRIBUTION OF CHEMICAL ELEMENTS IN TECHNOGENIC SILTS

Technogenic silts, which concentrate the bulk of pollutants entering the rivers of technogenic landscapes, are sources of secondary pollution of the water mass and toxic substances taken up by hydrobionts, because chemical elements and their compounds can be released from silts into the aqueous phase as a result of various processes occurring in sediments and at the near-bottom water–silt boundary. Silts can have a direct negative impact on living organisms. There are cases when, after termination of wastewater discharge into watercourses, technogenic silts were the source of pollutants entering surface water and taken up by hydrobionts. Therefore, it is particularly important to study the features of fixation and redistribution of chemical elements in technogenic silts.

Chemical Element Distribution in the Grain Size Distribution of Silts

The chemical element distribution in natural (background) channel alluvium is usually characterized by an increase in their specific concentrations from coarse-grained to finer sediment fractions (Kuznetsov, 1973; Lunev, 1967; Yanin, 2018). Analysis of the distribution of metals in the grain size distribution of technogenic silts in the Pakhra River (in the area 2 km below Podolsk) showed that almost all of them are characterized by a directional increase in their specific concentrations from the sand to the clay fraction, which is the main concentrator of most of the studied metals (Table 65) (Yanin, 2009c). Exceptions are iron, for which reduced contents have been established for the finer fractions (the main concentrator of Fe is the 0.10–0.01 mm coarse-grained silt fraction), and mercury, the highest levels of which are observed in the 0.25–0.1 mm fraction (fine-grained sand).

The technogenic anomalies of most metals occurred due to an increase in their specific concentrations in almost all of the selected fractions. The exceptions are Al, Ti, and Mn. In particular, the Al content in the sand fractions (compared with the local background) and Ti in coarse-grained sand hardly changed at all, while the Mn concentrations in the >0.01 mm fractions markedly decreased. In silts, the largest increases were in the concentrations of V, Mn, and Hg (in coarse-grained sand), Ti and Cr (in fine-grained sand), Fe, Zn, Ag, and Sn (in coarse-grained silt), Pb (in fine-grained silt), and Al (in clay fractions). For Ni, anomalies of practically equal intensity occurred in the >0.25 mm fractions. The peculiar distribution of Hg, Cr, Sn, and partly Pb should be noted, more intense anomalies of which were recorded in the sand fractions. Binocular microscope studies revealed that in native conditions, colloid particles adhere to large silt particles in a particular manner, which is clearly a result of sorption processes. It is possible that these particles (which were not destroyed during particle size analysis, performed without hard reagents) are

Table 65. Metals in grain size fractions of technogenic silts of Pakhra River

Metal	Fraction, mm										Ratio			
	I		II		III		IV		V		III : I	IIII : I	IIV : I	VV : I
	1–0.25		0.25–0.10		0.10–0.01		0.01–0.005		<0.005					
	C	K_C	C	K_C	C	K_C	C	K_C	C	K_C				
Al	18400	0.8	26900	0.9	52800	1.8	75600	1.8	87000	3.3	1.4	2.8	4.1	4.7
Mn	250	3.1	344	2.5	448	1.2	492	0.8	472	0.7	1.3	1.8	1.9	1.8
Fe	42800	24	57400	24	85800	36	18200	8.7	15400	24	1.3	2.0	0.4	0.3
Ti	305	0.9	663	2.7	2617	1.9	3414	1.5	4671	1.2	2.1	8.5	11.1	15.3
V	28	2.8	24	1.7	45	1.4	70	1.2	116	1.3	0.8	1.6	2.5	4.1
Cr	108	6.8	110	37	350	6	429	5.1	449	75	1.0	3.2	3.9	4.1
Ni	86	2.8	97	75	154	6.2	274	7	353	75	1.1	1.8	3.1	4.1
Zn	218	1.8	321	2.8	422	3.5	511	2.1	570	2.6	1.4	1.9	2.3	2.6
Ag	1.99	3	1.58	4	3.7	8	4.7	6.7	4.6	5.8	0.8	2.0	2.3	2.3
Sn	66	22	58	18	143	24	256	13.5	261	8.2	0.8	2.1	3.8	3.9
Hg	0.083	83	0.04	40	0.26	5.2	0.22	1.1	0.22	1.1	0.5	3.1	2.6	2.6
Pb	182	6.5	212	16.3	431	19.6	761	23	914	15.8	1.1	2.3	4.1	5.0

C, specific content in fraction, mg/kg; K_C, concentration coefficient with respect to content of sediments above city in this fraction (with respect to local background).

enriched in metals and create a pronounced effect. In addition, a certain part of coarse-grained silt particles form as a result of coagulation of fine SPM (enriched with mercury), which is especially characteristic of the near-impact zones of pollution sources (Yanin, 2002).

Analysis of the balance of rhe metal distribution in the grain size composition of technogenic silts of the Pakhra River showed that, for almost all of them, the main carrier is the coarse-grained silt fraction (0.10–0.01 mm), with which up to 50–70% of their total content is associated. On the one hand, this is due to the high share of this fraction in silts (obviously as a consequence of technogenic SPM input), and on the other, to its rather high specific metal concentrations. It is significant that above the city, this fraction (the amount of which averages 20%) is associated with up to 75–80% of the total amount of metals in channel sediments. In addition, compared with the local background, the value of the 0.25–0.10 mm fraction (as a carrier of chemical elements) significantly increased. Therefore, if in river sediments above a city, the share of this fraction (dominant in sediments is up to 43–47%) usually accounts for no more than 10–15% of the total amount of metals, then in the contaminated zone it is associated with up to 20–30% of the total the amount of metals in silts (the relative amount of this fraction in silts is usually no more than 30%). The sand fraction in silts accounts for an average of 10–20% of the total content of elements accumulating therein. Thus, the main metal concentrator in technogenic silts and background alluvium is usually the clay fraction; their main carrier is the coarse-grained silt fraction.

Table 66 shows the data on the mercury distribution in various grain size fractions of technogenic silts and background alluvium of the Nura River (Yanin, 1989, 1992). The results for background sediments confirm a well-known fact: a regular and significant increase in specific mercury concentrations from coarse to finer fractions. The main mercury concentrator in background alluvium is the clay fraction, and the main carrier is the medium-grained sand fraction, which is associated with more than 40% of the total metal content in sediments. A significant amount of mercury (up to 25–30%) is associated with the clay fraction, which is largely due to the high specific metal concentrations therein.

Mercury anomalies were manifested in silts due to a sharp increase in its contents in all fractions in virtually the entire studied area of the Nura River channel. However, the character of the distribution of this metal in the grain size distribution of silts differs from that in alluvium. Therefore, near the source of incoming runoff (i.e., in the zone of maximum pollution), its main concentrators are, as a rule, coarser sediment fractions. The intensity of technogenic anomalies in the coarser fractions is also more pronounced. As noted above, this peculiarity in the mercury distribution can be explained by the characteristics of the structural-aggregate composition of silts.

Note also that the upper layers of silts are a highly saturated suspension, consisting in large quantities of particles formed by coagulation and flocculation. It is possible that in various technological processes, as well as in sewage treatment, coarser particles are

Table 66. Mercury in various grain size fractions of sediments of Nura River

Distance from MWC, km	Horizon, cm	Coarse-grained sand		Large-grained sand		Medium-grained sand		Fine-grained sand		Very-fine-grained sand		Silt		Clay	
		mg/kg*	%**	mg/kg	%	mg/kg	%	mg/kg	%	mg/kg	%	mg/kg	%	mg/kg	%
3	2–20	100	0.4	600	3.02	1000	90.10	100	1.27	100	2.62	100	0.2	100	1.97
	20–40	1000	5.44	500	3.25	1000	7.84	400	4.26	300	7.96	500	52.95	400	18.3
	40–60	300	1.47	600	3.53	600	66.90	600	9.31	300	9.37	200	1.52	400	7.90
	60–80	300	0.69	100	0.25	500	28.14	500	31.38	300	20.79	200	9.96	100	8.79
	100–120	1500	1.64	1000	1.11	1000	45.61	1000	5.21	500	39.61	500	2.61	200	4.21
	120–140	100	1.84	300	2.93	300	3.42	300	12.92	300	6.65	300	48.9	400	23.34
9	40–60	–	–	50	3.71	10	5.81	20	13.41	100	17.81	100	11.31	100	47.95
	80–100	–	–	4	1.58	3	1.35	42	23.71	50	10.88	60	5.6	200	56.88
	120–140	–	–	1.2	2.42	0.5	1.13	3	9.0	20	22.24	42	5.41	100	59.80
32	20–60	–	–	1.2	8.65	0.45	11.02	0.75	19.01	1.4	8.91	1.2	5.12	5	47.29
105	20–40	–	–	4	2.20	1.3	10.26	3.5	28.47	3.5	7.53	5	7.42	8	46.12
	90–120	–	–	0.35	25.94	0.28	27.94	0.29	20.34	0.9	5.27	1	2.27	1	18.24
Background	0–20	0.010	0.72	0.031	20.21	0.12	41.15	0.26	5.39	0.50	2.83	0.46	1.55	0.80	28.15

* Specific mercury concentration in fraction, mg/kg; * share of mercury of gross per fraction, %.

enriched in mercury, which, due to the a greater hydraulic particle size, are deposited primarily in the near zone of pollution. Typically, the share of such fractions in the total mass of silts is insignificant (6% on average); therefore, the total amount of mercury associated with them is small (a few percent of the gross). The share of medium-, fine- and very-fine-grained sand fractions is already more significant. As a rule, they are the main carriers of mercury in river channels located near a pollution source.

With distance from the pollution source, there is a decrease in the gross mercury content and a change in the character of its distribution in grain size distribution of silts. The role of the main concentrators is played by finer-grained fractions: silt and clay, and the latter, in fact, are the main mercury carriers (frequently along with fine-grained and very-fine-grained sands). Apparently, this is due to a certain differentiation of channel sediments and farther migration of fine-grained particles—a well-known phenomenon described in the literature. It is interesting to note that quite contrasting technogenic anomalies have been recorded in the coarse-grained sand fraction along the entire flow. In the general case, it can be assumed that with distance from the source of pollution, the nature and characteristics of the mercury distribution in silts approach the background parameters.

Thus, in technogenic silts, geochemical anomalies of the studied heavy metals occurred (with varying degrees of intensity) due to an increase in their specific concentrations in all the isolated fractions. Almost all metals are characterized by a directional increase in their specific concentrations from the sand fractions to the clay fraction, which is their main concentrator. The exceptions are iron (the main concentrator is the coarse-grained silt fraction) and mercury (the concentrator fractions are fine- or medium-grained sand), which is due to the structural-aggregate composition of technogenic silts. Coarse-grained silt acts as the carrier fraction for most metals, which accounts for up to 50–70% of their total content, which is due to the high share of this fraction in sediments and the relatively high specific concentrations of metals therein. For mercury, depending on the distance from the pollution source and the silt horizon, the main carriers are medium- or fine-grained sand, and sometimes fine-grained sand or silt.

FORMS OF HEAVY METALS IN SILTS AND COMPOSITION OF SILT WATER

The speciation of metals concentrated in bottom sediments of waterbodies is quite diverse. Analysis of the published data shows that most studies mainly deal with the so-called mineralogical and geochemical speciation of chemical elements in various sediments identified by a formally genetic trait (Saet and Nesvizhskaya, 1974). In practice, it is better to distinguish between mobile, relatively mobile, and tightly bound forms of chemical elements. In this case, mobility refers to the ability of elements to be relatively actively involved in migration flows (e.g., to pass into a dissolved state with corresponding changes in environmental conditions, to be assimilated by living organisms, etc.). To transform strongly bound forms, a longer residence time in hypergenic conditions, more drastic changes in the latter, or the participation of a specific factor (e.g., acid rain) is necessary. Naturally, relatively mobile forms occupy a certain intermediate position. In native conditions, only geochemically active forms of metals are available to the biological food chain, especially easily mobile and some organomineral compounds. The significance of technogenic silts as secondary pollution sources is largely determined by the presence of geochemically active forms of pollutants. Below we consider the distribution and speciation of heavy metals in silts and the intensity of their concentration in silt water.

On the Pakhra River, samples of channel deposits (layer 0–30 cm) were collected in the following reference areas of the channel: I, above Podolsk (local background); IV, the mouth of Cherny Creek; V, VII, VIII, and XI, respectively 0.5, 5, 9, and 25 km below the mouth of Cherny Creek (Fig. 53). Silt water (from specially selected sediment samples) was separated with a centrifuge. River (bottom) water was collected with a GR-16 bottle on a rod. Water samples were passed through membrane filters with a pore diameter of 0.45 μm. To establish the speciation of metals in sediments, phase analysis was used, based on sequential processing of samples with selective extractants (Table 67). Metals in sediments, in extracts thereof, and in water samples (filtrates) were determined by atomic absorption.

Table 68 shows the data on the speciation of Cd, Cu, Ni, Pb in Pakhra bottom sediments; Table 69, the intensity of their concentration in technogenic silts in the zone of influence of Podolsk; Table 70, the metal content in silt and bottom water (Yanin, 2004a, 2016b). Above Podolsk (reference area I is the local background), the Pakhra's channel, as noted above, is covered mainly with medium-grained sands, close in composition to the background alluvium. Below the confluence with Cherny Creek (wastewater discharge areas), the structure of the studied segment of the Pakhra can be divided into three parts: near (areas IV–VII), middle (area VIII), and marginal (area XI). Here, technogenic silts are widespread in the Pakhra's channel, the specific contents of heavy metals in which usually significantly exceed the background levels.

Within the local background, the main forms of cadmium in channel alluvium are organic (37% of gross) and silicate (24.1%); the total share of its crystalline and silicate forms reaches 39%. Sorption–carbonate (most mobile) forms of cadmium (up to 58–68% of the gross) dominate in technogenic silts; its stable forms (silicate and, especially, crystalline) are subordinate (14–36 and 4.4–9%, respectively); the amount of organic compounds, despite the high content of organic matter in silts, is small (1.5–4%). With distance from the source of pollution in silts, there is a sharp decrease in the total cadmium content and a change in its speciation ratio. Therefore, in the marginal part of the observed technogenic sedimentation zone, there is a significant decrease in silts in the share of sorption–carbonate forms of cadmium and an increase in the organic and silicate forms. The most intense cadmium anomalies are manifested for its sorption–carbonate forms. Silt water is characterized by cadmium concentrations significantly exceeding its levels in bottom and background river waters. Of course, cadmium, which is present in silt water solution, is the most mobile part of its reserves in silts; it is capable of actively participating in migration flows and biogeochemical processes.

The above features of the distribution and fixation of cadmium in background alluvium and technogenic silts are quite natural. Thus, in natural waterbodies, a correlation between cadmium content (at very low total concentrations) and organic (primarily humic) matter is usually observed (Moore and Ramamurthy, 1987). This is clearly reflected in the significant share

Table 67. Sequential processing scheme for sediment samples with extraction of various forms of heavy metals

No.	Extractant	Predominant forms and their mobility
1	Acetate buffer mixture, pH 4.2	Sorption–carbonate; high migration mobility
2	Sodium pyrophosphate solution, pH ~ 13	Organic (metals associated with humic substances); increased mobility
3	0.15 N HCl Solution	Hydroxide (metals associated with amorphous Mn oxides, Fe oxides and hydroxides); increased mobility
4	6 N HCl solution	Crystalline (metals associated with crystalline oxides); relatively stable forms
5	Residue*	Silicate (metals included in lattices of detrital and clay minerals); stable forms

* Calculated by subtracting content of sum of previous forms from total metal concentration.

of organic forms of this metal in Pakhra background alluvium, in the organic matter of which the relative content (relative fraction) of humic substances exceeds 83%, whereas in technogenic silts, it is significantly lower: 33–46%.

Apparently, cadmium carbonate compounds are formed directly during wastewater treatment (to disinfect wastewater and sewage sludge (SS), quicklime, bleach, calcium hypochlorite, etc., are used) and then enter the river with SPM. For example, in Saransk SS, the share of cadmium forms extracted by acetate buffer extract reached 52.7% (with a gross content of 37.2 mg/kg) (Yanin, 1996).

The dominant forms of copper in bottom sediments of the background area are organic (46.4% of the gross) and sorption–carbonate (28.9%). The total share of stable (crystalline and silicate) forms of cadmium in channel alluvium is 15.3%; the number of hydroxide forms is small: up to 9.4%.

Thus, in the background conditions, copper concentrates in channel alluvium mainly in relatively mobile forms, but its specific gross contents are small, which indicates an insignificant role of bottom sediments in this metal's entry into the aqueous phase. This is confirmed by the low copper content in silt and bottom waters. In silts of the near zone of impact, the specific concentrations and relative share of hydroxide and silicate forms of copper species (up to 27.6–29.8 and 3.4–16.9%, respectively) increase, and the share of sorption–carbonate (up to 10.4–22.6%) and crystalline (up to 7.9–8.9)%) species decreases (with an increase in their specific concentrations). The spatially inhomogeneous distribution (on an insignificant linear extent of the channel segment) of both specific concentrations and relative share of sorption–carbonate and silicate forms of copper are noteworthy. In general, organic (33.9–38.9% of the gross) and hydroxide (27.6–29.8%) forms dominate in silts, and the content of sorption–carbonate forms (10.4–22.6%) is quite large. In silts that accumulate in the middle of the technogenic sedimentation zone (area V), the dominant forms of copper are already sorption–carbonate (40.1%) and, to a lesser extent, organic (24.6%). The largest technogenic anomalies of copper are manifested for its silicate forms. With distance from the source of pollution, there is not only a decrease in the total copper content in silts, but also an even greater (compared to the background) change in the balance of its species. Therefore, in the marginal part of the monitored technogenic sediment accumulation zone (area XI), a significant increase in the share of sorption–carbonate forms (from 10.4–22.6 near the city to 66.2%) is observed, along with a decrease in the organic (from 34–35 to 19.7%) and hydroxide (from 27.6–29.8 to 8%) forms. Technogenic copper anomalies occurred here only in its sorption–carbonate forms. As follows from this material, in silts, just like in background alluvium, mobile, geochemically active forms of copper also predominate, but, importantly, the specific content of its mobile forms is much higher in silts than in alluvium. Moreover, the specific concentrations of copper associated with sorption–carbonate, organic, or hydroxide forms exceed its gross background content. This indicates increased ecotoxicological hazard of silts and their role as a secondary source of copper pollution of the water mass, which, in particular, is confirmed by its intense concentration in silt water. Copper present in silt water in elevated concentrations represents the most mobile share of its reserves in silts, which can be a part of migration flows, participate in biogeochemical processes, and have a direct toxic effect on hydrobionts. In particular, the minimum copper concentrations for which acute toxic effects to aquatic organisms are possible have been estimated at 6–17 μg/L (Moore and Ramamurthy, 1987). The copper contents established in silt water exceed the indicated values.

The above features of the distribution and fixation of copper in background alluvium and technogenic silts are quite natural. Thus, according to (Mantoura et al., 1978), more than 90% of copper in them is associated with freshwater humic substances. It has been established that the organic matter composition in soddy-podzolic soils widespread in the Pakhra River basin and one of the main sources of its sedimentary material in background conditions are predominated

Table 68. Speciation of metals in Pakhra River bottom sediments

River area	Gross, mg/kg	Speciation									
		sorbate—carbonate		organic		hydroxide		crystalline		silicate	
		mg/kg*	%**	mg/kg	%	mg/kg	%	mg/kg	%	mg/kg	%
Cadmium											
I	0.54	0.07	13.0	0.20	37.0	0.06	11.1	0.08	14.8	0.13	24.1
IV	3.71	2.51	67.7	0.29	7.8	0.10	2.7	0.29	7.8	0.52	14.0
V	17.00	10.0	58.8	0.26	1.5	0.29	1.7	0.75	4.4	5.70	33.6
VII	6.47	4.20	64.9	0.10	1.5	0.11	1.7	0.33	5.1	1.73	26.8
VIII	1.80	1.08	59.8	0.07	4.0	0.03	2.1	0.11	6.0	0.51	28.1
XI	0.50	0.19	37.8	0.06	13.0	0.02	4.0	0.05	9.0	0.18	36.2
Copper											
I	40	11.56	28.9	18.56	46.4	3.76	9.4	5.56	13.9	0.56	1.4
IV	190	42.94	22.6	64.41	33.9	52.63	27.7	15.01	7.9	15.01	7.9
V	530	55.12	10.4	182.85	34.5	157.94	29.8	44.52	8.4	89.57	16.9
VII	120	25.44	21.2	46.68	38.9	33.12	27.6	10.68	8.9	4.08	3.4
VIII	90	36.09	40.1	22.14	24.6	12.33	13.7	5.85	6.5	13.59	15.1
XI	48	31.77	66.2	9.45	19.7	3.84	8.0	2.37	4.9	0.57	1.2
Nickel											
I	24	9.29	38.7	4.63	19.3	2.76	11.5	4.94	20.6	2.38	9.9
IV	67	35.31	52.7	5.70	8.5	12.39	18.5	8.17	12.2	5.43	8.1
V	157	55.11	35.1	13.34	8.5	24.65	15.7	18.37	11.7	45.53	29
VII	45	22.23	49.4	4.32	9.6	6.93	15.4	6.35	14.1	5.17	11.5
VIII	35	13.30	38.0	0.49	1.4	5.32	15.2	5.21	14.9	10.68	30.5
XI	32	14.30	44.7	4.2	13.1	5.6	17.5	6.18	19.3	1.72	5.4
Lead											
I	35	4.24	12.1	1.05	3.0	8.50	24.3	14.81	42.3	6.40	18.3
IV	357	99.96	28.0	6.43	1.8	138.87	38.9	69.62	19.5	42.12	11.8
V	210	73.50	35.0	6.72	3.2	65.10	31.0	44.10	21.0	20.58	9.8
VII	140	55.86	39.9	4.34	3.1	40.74	29.1	28.00	20.0	11.06	7.9
VIII	70	35.70	51.0	1.40	2.0	16.10	23.0	10.85	15.5	5.95	8.5

* Specific concentration, mg/kg; ** relative share of total content, %.

by humic acids (up to 68–69% of total organic matter (Aleksandrova, 1946), while in soils, for copper, as a rule, the value of organic forms is high (Kabata-Pendias and Pendias, 1989). All of this is clearly reflected in the higher relative content of organic forms of this metal in Pakhra background alluvium, in the organic matter of which the share of humic substances exceeds 83%, while in technogenic silts, it decreases to 33–46%. It is indicative that in the SPM of two Canadian rivers (the St. Francis and Yamask, which flow through southern Quebec), a significant part of copper consisted of organic forms (respectively, 31 and 52%) (Tessier et al., 1980). The significance of carbonate and hydroxide forms of copper in Pakhra technogenic silts are confirmed by the very high contents of carbonate minerals and amorphous iron hydroxides in the latter.

Within the background area, the main forms of nickel in sediments are sorption–carbonate (38.7%), crystalline, (20.6%) and organic (19.3%). The shares of its hydroxide and silicate forms are 11.5 and 9.9%, respectively. Thus, in the background alluvium, nickel (like copper) is concentrated mainly in relatively mobile forms, but its total content in alluvium and concentration in pore water is small, which points to the insignificant role of bottom sediments in this metal's entry into the aqueous phase. In silts forming in the near sedimentation zone, nickel technogenic anomalies are most heavily manifested in silicate, hydroxide, and sorption–carbonate forms. This is

Table 69. Intensity of heavy metal concentrations in technogenic silts of Pakhra River*

River area	Speciation				
	sorbate–carbonate	organic	hydroxide	crystal	silicate
			Cadmium		
IV	35.8	1.5	1.7	3.6	4.0
V	142.8	1.3	4.8	9.4	43.8
VII	60.0	0.5	1.8	4.1	13.3
VIII	15.4	0.35	0.5	1.4	3.9
XI	2.7	0.3	0.3	0.6	1.4
			Copper		
IV	3.7	3.5	14.0	2.7	26.8
V	4.8	9.9	42.0	8.0	159.9
VII	2.2	2.5	8.8	1.9	7.3
VIII	3.1	1.2	3.3	1.1	24.3
XI	2.7	0.5	1.0	0.4	1.0
			Nickel		
IV	3.8	1.2	4.5	1.6	2.3
V	5.9	2.9	9.0	3.7	19.1
VII	2.4	0.9	2.5	1.3	2.2
VIII	1.4	0.1	1.9	1.1	4.5
XI	1.5	0.9	2.1	1.3	0.7
			Lead		
IV	23.6	6.1	16.3	4.7	6.6
V	17.3	6.4	7.7	2.9	3.2
VII	13.2	4.1	4.8	1.9	1.7
VIII	8.4	1.3	1.9	0.7	0.9

* In concentration coefficients with respect to background for specific forms.

reflected as an increase in the share of these forms in silts and, accordingly, a decrease in the share of organic and crystalline forms. In general, the balance of nickel species in silt differs from that in background alluvium. The spatially nonuniform distribution of both the specific concentrations of nickel and the relative share (in the overall balance) of its sorption–carbonate and silicate forms is noteworthy. Nevertheless, in silts, sorption–carbonate forms of nickel predominate, virtually within the entire monitored technogenic sedimentation zone: 35.1–52.7% of the gross. Thus, mobile forms of nickel also dominate in silts; however, most importantly, their specific concentrations are much higher than in background alluvium (often the specific concentrations of nickel associated with sorption–carbonate, organic, or hydroxide forms exceed its total background content). This, in addition to the high metal content in silt water, indicates the ecotoxicological significance of silts and their potential role as a secondary source of pollution of the water mass.

The leading role of sorption–carbonate forms of nickel fixed in channel sediments, which increases under pollution conditions, is quite natural. The carbonate compounds of this metal obviously form during the wastewater treatment of at sewage treatment plants and enter the river as part of SPM. In particular, in SS generated at city wastewater treatment plants, during joint treatment of industrial and domestic wastewater, the share of nickel forms recovered by ammonium acetate extract reached 55.6% (for a gross content of 320 mg/kg); the share of strongly bonded forms was 20.1%; organic, 24.3% (Yanin, 1996). It is also known that bonding of nickel with iron and manganese oxides, which are its active sorbents, plays an important role in the behavior of this metal in aqueous systems (Linnik and Nabivanets, 1986; Moore and Ramamurthy, 1987). Silts forming in the Pakhra River are distinguished by high contents of carbonate minerals and amorphous iron hydroxides. The higher relative content of organic forms of nickel in background alluvium is quite explainable by the well-known role of its complexation with humic substances (Linnik and Nabivanets, 1986). As noted above, the organic matter of soddy-podzolic soils widely encountered in the Pakhra River basin and one of the main sources of its sedimentary material in background conditions are dominated by humic acids (up to 68–69% of total organic matter) (Aleksandrova, 1980). This, of course, is reflected in the higher relative content of organic forms of this metal in Pakhra background alluvium, in the organic matter of which the share of humic substances exceeds 83%, while in technogenic silts, it decreases to 33–46%. According to (Kabata-Pendias and Pendias, 1989), nickel in upper soil horizons is present mainly in organic forms, some of which can be represented by readily soluble chelates, which predetermines their active removal and entry into waterbodies. Technogenic silts forming in the Pakhra River below Podolsk are also distinguished by increased contents of fine-grained particles and clay minerals, which likely indicates sorption forms of this metal.

Table 70. Heavy metals in silt and bottom waters of Pakhra River, μg/L

River area	Silt water	Bottom water
Cadmium		
I	0.5	0.2
IV	1.4	0.9
V	3.6	1.0
VII	2.6	1.8
VII	2.6	2.0
XI	1.8	0.5
Background*	0.133	
Copper		
I	4	3
IV	18	33
V	36	23
VII	60	19
VII	32	13
XI	26	9
Background*	7.62	
Nickel		
I	4.2	3.8
IV	17.5	85.8
V	83.0	54.0
VII	59.7	18.6
VII	31.9	12.6
Background*	2.5	
Lead		
I	5.12	3.21
IV	73.0	19.0
V	60.0	16.6
VII	32.0	12.0
VII	12.0	3.8
Background*	2.17	

* In waters of Moscow oblast rivers.

Within the local background, a significant share of lead in channel sediments is represented by its stable (crystalline and silicate) forms (in total, more than 60% of the gross), and the relative share of the most mobile (sorption–carbonate) forms is small (about 12% of the total). In the silts that form in the Pakhra River, in the zone of influence of Podolsk, lead predominantly accumulates (up to 70–76% of the gross) in mobile and relatively mobile (mainly in sorption–carbonate and hydroxide) forms. The most stable forms of lead—crystalline and especially silicate–in the zone of influence of the city are of subordinate importance (in total, no more than 24–31% of the total content). It is important to note the following. First, in technogenic silts, the specific concentrations of sorption–carbonate and hydroxide forms of lead are many times higher than the content of similar forms in background alluvium. Second, in the pollution zone, the specific concentrations of these forms often exceed the gross background level. Third, the lead levels in silt water are significantly higher than their concentrations in bottom water. All this, together with a high total lead content, a priori indicates the increased ecotoxicological hazard of technogenic silts and their role in this metal's entry into to the water mass and its uptake by aquatic organisms. During channel migration, not only does a regular decrease in the gross concentration of lead occur in technogenic silts of the Pakhra River, but also a change in the balance of its speciation, which is clearly associated primarily with the transformation of silts by hypergenic (diagenetic) processes, and to a lesser extent, with the influence of additional sources of sediment supply into the river channel (both natural and technogenic). Therefore, downstream (from Podolsk), there is a marked decrease in Pakhra channel sediments in the relative share of hydroxide forms (from 39 to 23%) and a significant increase in sorption–carbonate forms of lead (from 28 to 51%). This, in part, may be related to the breakdown of amorphous ("fresh") iron and manganese oxides and hydroxides, as well as with the increasing role of sorption processes in the deposition of metal transported by the water flow. The relative content of organic compounds of lead varies from 1.8 to 3.2%, which may be due to variations in the concentration and composition of organic matter present in technogenic silts. The fact of a certain decrease (downstream) in the relative content of crystalline (from 19–21 to 15%) and silicate (from 11.8 to 8–8.5%) forms of lead is indicative of long-range transport of technogenic sedimentary material entering the river with runoff. The relatively weak correlation of lead with organic matter is noteworthy, which is apparently quite natural. For example, even in lacustrine sediments rich in organic matter, only about 5–10% of lead is bound with organic matter, mainly with humic acids (Nriagu and Coker, 1980). It is also known that in soils, lead is mainly associated with manganese and iron oxides, forms carbonates, and is sorbed by clay matter (Kabata-Pendias and Pendias, 1989). The formation of sorption species of lead is facilitated by the peculiar grain size distribution of technogenic silts, in which the share of clay and silt (<0.01 mm fraction) is 12–16%; the <0.005 mm fraction, up to 5–8%. These particles are not only the main concentrating fractions, but also the lead-carrier fractions in technogenic silts. The significance of sorbate–carbonate and hydroxide forms of copper in technogenic silts of the Pakhra are confirmed by the very high contents of carbonate minerals and amorphous iron hydroxides in the latter. Lead carbonate compounds also undoubtedly form during sewage treatment at treatment plants and they enter the river as part of wastewater SPM.

The observed spatial changes in the distribution of the studied heavy metals and the balances of their forms in Pakhra sediments below Podolsk are caused not only by the blending of technogenic material with natural sediments, but also by the hypergene transformation of silt material. The results also indicate the important role of sorption processes in the deposition of heavy metals transported by water, especially with distance from the source of pollution. Judging from this, near the city, hydraulic sedimentation of technogenic SPM, in which metals are present in "primary" (e.g., carbonate) forms generated during wastewater treatment at city treatment plants, is of particular importance.

To study the forms of mercury in technogenic silts and SPM of the Nura River, phase chemical analysis was used according to the following scheme (Table 71). Naturally, for the indicated sequential extraction of various mercury compounds, the geochemical interpretation of the analysis results is, to a certain extent, conditional. However, in mass studies, the obtained material quite objectively reflects the real speciation ratio in terms of geochemical activity.

Table 72 shows the results of studying the forms of mercury in silt samples collected from different parts of the technogenic dispersed flow: head, middle, and marginal (Yanin, 1989, 1992). For an overall high concentration of Hg in silts, anomalies manifested themselves in connection with an increase in the specific concentrations in all liberated forms, but the metal concentration intensity is different. The most dramatic technogenic Hg anomalies occurred in the oxide (K_C from 345 to 11931), strongly bound (up to 1614), and elemental (up to 3182) forms. The concentration intensity of Hg associated with the sulfate form is small (K_C on average 2–3). Identification of this form is the most arbitrary due to the relatively high error and insignificant yield of this fraction during phase analysis. Apparently, these mercury compounds combined in this unstable form (sulfate, readily soluble organic, etc.) play an insignificant role in the overall speciation balance. However, it should be noted that despite the insignificant share in the total balance, their specific concentrations are several times higher than the total Hg content in background alluvium. Moreover, with distance from the source of pollution, there is a tendency toward an increase in both their specific concentrations and relative abundance, which clearly indicates ongoing transformation from stabler to highly mobile forms in silts.

Hg oxides, which are generally unstable, especially those associated with iron and manganese oxides and hydroxides, predominate in the overall speciation balance (on average, in the near zone, ~58%). However, a rather pronounced heterogeneous distribution of both the relative (from 25 to 75%) and specific (from 15.2 to 525 mg/kg) contents of this form in the silt profile has been recorded. With increasing distance from the source of pollution, a certain relative increase (on average, up to 70 and 63%, respectively) of the share of oxide forms sharply predominating over other forms is noted. The elemental form (represented by atomic mercury) in the near zone of impact averages 19% of the total content. In the silt profile, its share, as well as specific content levels, also vary irregularly. With distance from the city, the specific contents and relative share of elemental mercury in the general speciation balance decrease markedly. Thus, the share of this form in the middle and peripheral parts of the studied channel segment are on average about 10 and 13%, respectively, which is a logical consequence of various transformation processes for mercury compounds. The strongly bonded forms, which are apparently represented by mercury sulfide compounds, as well as calomel, are on average 19–22%. As in the case with other forms, irregular changes in both the relative and absolute content in the technogenic silt profile have been recorded.

It should be noted that, in the general case, a fairly good similarity is observed in the structure of the mercury speciation balance in technogenic silts and SPM (Fig. 44). This indicates the leading role, especially in recent years, of suspended solids in forming contrasting lithochemical dispersed mercury flows in bottom sediments. The observed differences are a natural consequence of the transformation processes occurring both in silts and SPM.

The results of studying the mercury distribution in silt water showed their marked enrichment in this metal, and its concentration is stably higher than in river water (Table 73). Apparently, at the water–silt boundary there is a constant directional concentration gradient of dissolved forms of mercury from sediments to water. In this case, there is a direct dependence of the mercury content in silt water on its concentration in silts.

Thus, a significant portion of mercury in silts accumulates in relatively mobile forms. With distance from the source of pollution, the gross mercury content and specific concentrations of its various forms decrease.

Table 71. Scheme of phase analysis of technogenic silts and SPM (Yanin, 1992)

Sequential treatment with solvents	Conditional name of species	Mineralogical and geochemical interpretation of species	Geochemical behavior
0.1 N HCl	Sulfate	Mercury sulfate, readily soluble organic compounds, mercury(II) chloride	Unstable, highly mobile
6 N HCl	Oxide	Oxides, hydroxides, mercury oxychlorides; mercury associated with iron oxides and hydroxides, possible sorbed forms	Low-stability, mobile
HNO_3 concentrated	Elemental	Metallic (atomic) mercury	Relatively mobile
Residue	Strongly bound	Mercury sulfide compounds, mercury(I) chloride	Stable, but with evidence of their instability, in particular, oxidation of sulfides is possible in presence of oxidizing agents

Table 72. Mercury speciation in technogenic silts of Nura River

Sampling site	Horizon, cm	Gross, mg/kg*	Sulfate		Oxide		Elemental		Residue (tightly bound)	
			mg/kg**	%***	mg/kg	%	mg/kg	%	mg/kg	%
1.5 km below MWC	0–20	21	0.06	0.28	15.2	72.38	4.8	22.86	0.94	4.48
	20–40	72	0.1	0.14	20.8	28.88	27.7	38.47	23.4	32.51
	40–60	280	0.7	0.25	180	64.28	15	5.36	84.3	30.11
	60–80	169	0.1	0.06	62.6	37.05	35.3	20.88	71	42.01
	80–100	117	4.5	3.84	46.5	39.75	31	26.5	35	29.91
	100–120	62	0.1	0.17	15.6	25.57	25.6	41.97	19.7	32.29
	120–140	690	0.1	0.02	470	68.11	130	18.84	89.9	13.03
	140–160	310	0.1	0.03	210	67.75	33	10.64	66.9	21.58
	160–180	680	0.2	0.03	525	77.21	140	20.58	14.8	2.18
	180–200	340	0.1	0.03	250	73.52	37	10.89	52.9	15.56
	200–220	70	0.2	0.29	36.5	52.14	12.7	18.14	20.6	29.43
	220–240	35	0.02	0.06	26	74.29	8.9	25.42	0.08	0.23
	240–260	230	0.1	0.04	150	65.22	9.9	4.3	70	30.44
	260–280	32	0	0	24	75	3	9.37	5	15.63
40 km below MWC	0–30	22	0.1	0.45	14.1	64.09	1.6	7.28	6.2	28.18
	30–60	19	0.2	1.05	15.1	79.47	1.4	7.36	2.3	12.12
	0–30	20	0.5	2.5	13	65	1.9	9.5	4.6	23
	30–60	22	0.4	1.81	16	72.73	3.1	14.09	2.5	11.37
90 km below MWC	0–30	60	1.4	2.34	40	66.66	6	10	12.6	21
	30–60	29	0.6	2.07	17.1	58.96	4.2	14.49	7.1	24.48

* Background total mercury content, 0.044 mg/kg; ** specific concentration, mg/kg; *** share of form out of gross content, %.

There is a regular change in the ratio of various forms of mercury downstream, manifested as a certain increase in the relative share of oxide forms, to a lesser extent, sulfate forms, as well as in a decrease in the share of elemental mercury. This indicates the geochemical transformation of forms of mercury as it migrates. The share of strongly bound forms of mercury usually does not exceed 25–30%. The mobility coefficients for mercury (the ratio of mobile and tightly bound forms) for the entire silt mass are quite large. In addition, the total Hg content in silts is so significant that even a low level of mobile forms will determine their ecotoxicological hazard. There is a direct dependence of Hg levels in silt water on its con-

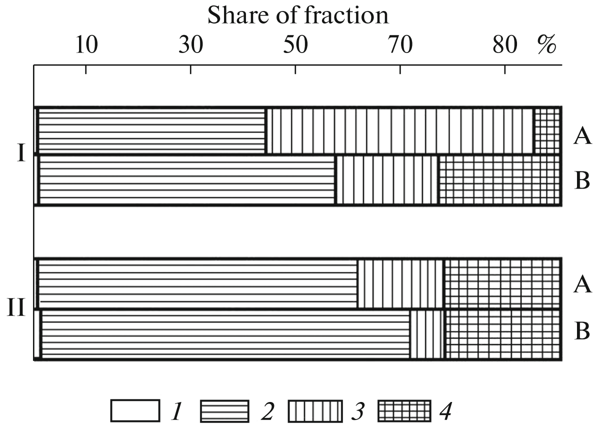

Fig. 44. Ratio of mercury speciation in SPM (A) and technogenic silts (B): I, MWC, II, Nura River 16 km below; species: (*1*) sulfate; (*2*) oxide; (*3*) elemental; (*4*) strongly bound.

tent in silts, which also indicates the probability of the metal entering the water column.

EXCHANGEABLE CATIONS IN TECHNOGENIC SILTS

There is virtually no information in the literature on the composition of exchangeable cations of river sediments, technogenic silts in particular. The author was able to study the composition of the exchange complex of background alluvium, sewage sludge (SS), and technogenic silts (Tables 74, 75; Fig. 45) (Yanin, 2016a).

Silts and SS are characterized (compared to background alluvium) by high values of dry residue, high exchange acidity, and significant contents of exchangeable ions. The cationic exchange capacity of background alluvium is low, 4.84 mg-eq/100 g of sediment; for technogenic formations, it increases three to ten times, in some cases reaching 38–41 mg-eq/100 g for silts and 44.25 mg-eq/100 g for SS.

The highest cation exchange capacity values are naturally characteristic of sediments with low pH values. Both in the background alluvium and technogenic sediments, calcium (68–81% of total) dominates in the composition of exchangeable cations; the share of exchangeable magnesium is also substantial (32–36% of total). It is significant that the amount of exchangeable NH_4^+ significantly exceeds that of exchangeable sodium and potassium (sometimes by an order of magnitude). Technogenic formations are also distinguished by an elevated (two to ten times) NO_3^- content. The observed variations in the absorption capacity values are due to spatial differences in the material (especially the grain-size and mineral) composition of sediments, as well as the amount and group composition of organic matter. Apparently, the main carriers of the adsorption properties of technogenic silts are amorphous and organic matter, iron hydroxides, and carbonate and (in some cases) clay minerals.

Table 73. Mercury in technogenic silts and silt and surface water of Nura River

Sampling site (below Temirtau)	Water, μg/L		Silt, mg/kg
	silt	surface	
1.5 km	4.90	4.0	500
9 km	2.70	1.1	100
17 km	2.60	1.9	78
31 km	0.65	0.5	33

In the general case, technogenic silts are characterized by a quite high cation absorption (exchange) capacity, from 14.19 to 41.36 mg-eq/100 g (average 29.91). For comparison, the cation exchange capacity of the silt fraction (<0.001 mm) of soddy-podzolic soils widely encountered in the Pakhra River basin ranges from 36 to 56 mg-eq/100 g (Gorbunov, 1963). The cation exchange capacity of kaolinite is 3–15; montmorillonite, 80–150; illite, 10–40; vermiculite, 100–150; chlorite, 10–40; and organic matter, 150–500 mg-eq/100 g (Grim, 1967); sediments in the Damodar River (India), 12.5; in the Hudson River (United States), 5.4–24.5 mg-eq/100 g (Babenkov, 1977).

Thus, technogenic silts and SS are characterized (compared to natural alluvium) by high values of dry residue, high exchange acidity, and significant contents of exchangeable ions. Whereas the cationic exchange capacity of background alluvium is 4.84 mg-eq/100 g of sediment, technogenic formations increase by three to ten times, reaching 38–41 mg-eq/100 g for technogenic silts and 44.25 mg-eq/100 g for SS. The highest cation exchange capacity values are naturally characteristic of sediments with low pH values. Calcium dominates in all sediments in the composition of exchangeable cations (68–81% of total), and the share of exchangeable magnesium is also significant (32–36%). The amount of exchangeable NH_4^+ significantly exceeds the content of exchangeable sodium and potassium. Technogenic formations are distinguished by an elevated (by two to ten times) NO_3^- content. The main carriers of the adsorption properties of technogenic silts are amorphous and organic matter, iron hydroxides, and carbonate and clay minerals.

SECONDARY TRANSFORMATIONS OF SILTS AND POLLUTANT RELEASE PROCESSES

The migration mobility, solubility, and bioavailability of chemical elements associated with technogenic silts can be activated by various factors and phenomena (decrease in pH, changes in redox conditions, formation of organic complexes, increase in water

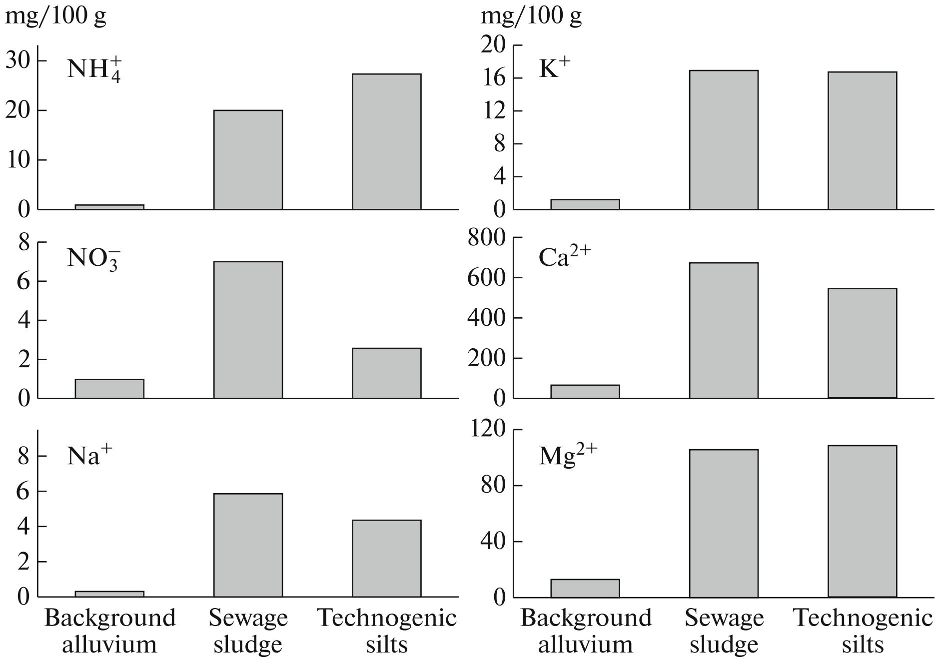

Fig. 45. Exchangeable ions in different sediments.

salinity, etc.). Primarily, secondary silt transformations may be associated with the transformation of their organic, carbonate, and clay components; the conversion of iron compounds; the formation of "fresh" Fe, Mn, and Al hydroxides and their hydrosols and secondary aluminosilicates and amorphous minerals; silts losing unbound water as they compact; the relative increase in the content of stable titanium minerals; and blending of technogenic material with natural sedimentary material.

The transition of Fe and Mn protoxides to mineral oxides of the same elements as a result of redox processes cannot be excluded either. For Eh values less than 200 mV and pH 6–8 (which can be quite realistic in the silt sequence), Fe and Mn hydroxides can be reduced, with the formation of lower valence com-

Table 74. Exchangeable ions in channel sediments and urban SS

River (city)	pH	Dry residue, mg/100 g	mg-eq/100 g						Exchange acidity, mg-eq/100 g
			NO_3^-	NH_4^+	Na^+	K^+	Ca^{2+}	Mg^{2+}	
Background alluvium									
Pakhra, upper reaches	7.4	11.8	0.01	0.05	0.01	0.03	3.62	1.13	<0.009
Urban SS									
(Podolsk)	4.8	400.0	0.11	1.11	0.26	0.44	33.68	8.76	0.605
Technogenic silts									
Muranikha	4.7	276.5	0.09	1.87	0.07	0.09	25.70	6.99	0.639
Petritsa, upper reaches	4.6	396.3	0.04	1.53	0.19	0.43	27.45	9.01	0.675
″	6.2	320.3	0.05	1.46	0.11	0.35	33.18	6.25	0.153
Petritsa (Klimovsk)	7.4	301.3	0.05	0.24	0.11	0.40	27.45	6.74	0.054
″	7.4	139.8	0.01	0.10	0.02	0.06	10.51	3.50	0.036
″	7.4	197.5	0.03	0.14	0.04	0.15	13.97	4.01	0.027
″	7.3	275.5	0.05	0.44	0.05	0.24	26.95	5.24	0.072
Petritsa, mouth	6.6	186.5	0.02	0.36	0.04	0.14	16.72	6.99	0.087
Average	6.5	261.7	0.04	0.77	0.08	0.23	22.74	6.09	0.22

Table 75. Exchangeable cations in Pakhra River background alluvium, in technogenic silts of its tributaries, and in Podolsk SS

Place	Total cations mg-eq/100 g	In % of total				
		NH_4^+	Na^+	K^+	Ca^{2+}	Mg^{2+}
Background alluvium						
Pakhra, upper reaches	4.84	1.03	0.21	0.62	74.79	23.35
Urban SS						
(Podolsk)	44.25	2.51	0.59	0.99	76.11	19.80
Technogenic silts						
Muranikha	34.72	5.39	0.20	0.26	74.02	20.13
Petritsa, upper reaches	38.61	3.96	0.49	1.11	71.10	23.34
"	41.35	3.53	0.27	0.85	80.24	15.11
Petritsa (Klimovsk)	34.94	0.69	0.32	1.14	78.56	19.29
"	14.19	0.70	0.14	0.42	74.07	24.67
"	18.31	0.76	0.22	0.82	76.30	21.90
"	32.92	1.33	0.15	0.73	81.87	15.92
Petritsa, mouth	24.25	1.49	0.16	0.58	68.95	28.82
Average	29.91	2.23	0.24	0.74	75.63	21.15

pounds of these metals, which have a higher migration ability. At the same time, other metals sorbed by hydroxides are capable of passing into solution. In the upper silt sequence, it is possible to expect the development of microbiological processes capable of influencing a change in physicochemical conditions and chemical redistribution in the sequence and between silt and bottom water. Microorganisms, as is well known (Gadd, 2001), play an important role in the fate of many chemical elements in the environment and in the transformation of their forms; they influence redistribution between the soluble and insoluble phases of pollutants. The relatively slow salinity of the organic component of silts should contribute to the formation of mobile metal compounds, which, e.g., can be taken up by aquatic vegetation or released into silts and then into river water. The activity of aquatic organisms, especially benthic, plays a certain role in increasing the migration capacity of chemical elements associated with bottom sediments.

The formation of silts under conditions of a hydrodynamically active river channel and, as a rule, for a comparatively small river depth governs the physicochemical instability of the sedimentation setting, which is complicated by the seasonal factor, and the development of redox processes, which go toward establishing equilibrium between the oxidized mineral component of silts and organic matter, which acts as a reducing agent in these processes. As these processes occur, the organic and inorganic components of sediments change. This does not exclude the active remobilization of heavy metals from silts into water.

Deeper silt layers host anoxic horizons. The occurrence of gley and even (especially in winter) hydrogen sulfide settings is not excluded. The development of reducing (gleying) conditions is facilitated by the high content of clay fractions in sediments and (in backwaters) slow water exchange. As technogenic SPM settles to the bottom, the intensity of its oxidation decreases, which in turn is associated with a decrease in the intensity of turbulent water mixing in immediate proximity to the surface of river sediments. In such cases, dissolved oxygen in water is undoubtedly fixed by the upper silt layer, without hardly entering their deeper layers, which may contribute to the occurrence of reducing conditions. Under oxygen deficiency conditions in silts enriched in organic matter and having elevated sulfur contents, sulfate reduction can occur, with the formation of hydrogen sulfide (especially in winter) and metal sulfides. The occurrence (primarily in winter) of hydrogen sulfide conditions, even sporadically, in silt strata is probable. Under such conditions, microbial dechlorination of organochlorine compounds (Opekunov, 2005), which are almost always present in technogenic silts, is quite active in sediments.

The data on the forms of Cd, Cu, Ni, Pb and their distribution in technogenic silts make it possible to outline the main groups of geochemical processes that can facilitate the migration of metals into the aqueous phase and uptake by hydrobionts (Yanin, 2015): (1) a decrease in pH (dissolution of carbonates and sorbed compounds); (2) gleying in places of heavy silt accumulation (breakdown of Fe–Mn oxides); (3) microbial activity (decomposition of organic compounds and Fe–Mn oxides); (4) an increase in river water salinity, especially due to chlorides, and the influx of various complexing agents into rivers, primarily surfactants (desorption and ion exchange processes); (5) stirring of bottom sediments (release of metals from the solution of silt water and fine-grained particles); (6) the activity of benthic organisms and macrophytes (uptake of metals from silt water and silts). These processes and phenomena are quite typical of rivers and are particularly pronounced in technogenic conditions (sharp changes in acid–base and redox conditions, channel areas with heavy silt accumulation, the flow of more saline wastewater with a high chloride content, high concentrations of various complexing agents, especially surfactants, etc.). Mercury, which is one of the soluble compounds, is capable of active migration. Mercury sulfide compounds, differing by a high stability, can nevertheless be gradually oxidized by a number of oxidizing agents. It is known that under reducing conditions and at pH 6–8, iron and manganese hydroxides are actively reduced, with the formation of low-valence compounds of these elements with a much higher migration ability. At the same time, mercury bound to them passes into solution. Thus, in some areas of the Nura River channel, a simultaneous increase in the contents of dissolved forms of iron, manganese, and mercury was recorded.

One of the factors contributing to chemical elements passing into water is a change in hydrodynamic conditions. The predominant relationship between chemical elements and fine-grained particles of technogenic silts in most of the studied area indicates their potential migration ability. When the flow velocity increases (and as a result of the activity of benthic organisms), the upper silt layer is disturbed, and the material passes into suspension and eventually comes into closer contact with water, which can lead to desorption of pollutants. In addition, the latter can pass out of silt water residing in the disturbed sediments. Resuspension of sediments under pollution conditions is considered the most important factor in the redistribution of pollutants associated with them (Young et al., 1992). Changes in water viscosity due to the occurrence of even a slight positive temperature gradient, which is typical of polluted parts of rivers due to the influx of warmer wastewater (especially in the cold period), can also lead to increased transport capacity. All these processes will contribute to the migration of sediments downriver, the release of pollutants into the water column, and their influx to the floodplain during irrigation and flooding.

Beyond the hydrodynamic factor, the migration flow of various pollutants from bottom sediments into water is largely determined by concentration diffusion. Molecular diffusion of the dissolved compounds of many elements is a universal process by which they are released from sediments into water; it takes place in nearly every waterbody and is maintained by a concentration gradient of matter near the water–bottom boundary. For most components, this gradient is observed even in natural waterbodies with low mercury concentrations in sediments and water. This, e.g., was observed under natural conditions of a background reservoir (Lake Glubokoe, Moscow oblast) for a fairly wide group of chemical elements and their compounds. In particular, a study of the heavy metal distribution at the water–sediment interface showed that many of them are concentrated in silt water. (Yanin et al., 1986). This governs the existence of a rather distinct gradient in the concentration of matter near the water–bottom boundary.

Gas formation processes occurring in a clay sediment sequence can play a certain role in the release of chemical elements and their compounds into the water mass (Fendinger et al., 1992). The presence of significant amounts of organic matter in technogenic silts and their breakdown predetermine the formation of free (spontaneous) gases in such sediments (CO_2, H_2, N_2, H_2S, CH_4, NH_3, and possibly H_2). Therefore, under mechanical impact on technogenic silts (e.g., when they are sampled with a corer), intensive bottom gas release and the appearance of gas bubbles on the water surface are always observed.

Thus, there is every reason to believe that technogenic silts are significant secondary sources of various pollutants entering the water mass and taken up by biota.

CONCLUSIONS

Under natural conditions, the formation, morphology, and material composition of channel alluvium is largely due to the direction and intensity of erosion–accumulation processes occurring within the catchment area and in river channels, by which sedimentary material enters the watercourse. The main sources of the latter are soils and rocks. Usually, channel alluvium is represented by lithogenic facies, which is mainly the result of mechanical accumulation of sedimentary material in channels, the lithological, mineralogical, and geochemical characteristics of which are determined by the peculiarities of the geological structure and vegetative soil of the catchment areas. Almost everywhere, there is a limited set of lithological–petrographical types of channel sediments, characterized by dominant monomineralic quartz sands with a high degree of differentiation and elevated silica contents. The concentrations of chemical elements in the channel alluvium of the lowland rivers are within their regional and global distribution limits in sedimentary rocks and the lithosphere.

The formation of water runoff in technogenic landscapes is determined by their hydrological features, which reflect the specifics of the water balance of economically developed areas, which in turn are due to climatic factors, the peculiarity of the formation conditions and the surface, groundwater and subsurface flow regimes, and the extent of water consumption and wastewater disposal. An important feature of such areas is large water volumes in relatively small areas, which, after use for economic needs, acquire other physicochemical properties, contain huge masses of technogenic sedimentary material, and, as a rule, are discharged into the hydrological network. Solid runoff moduli here increase (compared with local and zonal values) by one to two orders of magnitude. The supply of technogenic sedimentary material to rivers is distinguished by a specific material composition and high concentrations of many chemical elements and their compounds.

The input of significant amounts of technogenic sedimentary material into rivers is reflected in alluvial sedimentation processes and leads to the development of widespread areas with a new type of channel sediments: technogenic silts. The most important morphological properties of silts that are stratified at places of their heaviest accumulation, owing to the conditions of their sedimentation and secondary transformations, have a dark gray or black color, a specific smell, viscous or soft plastic consistency, and high concentrations of fine-grained (silty clay) particles and organic matter. These properties are relatively stable both in the silt sequence, the vertical thickness of which varies from 0.2–0.5 to 2–3.5 m, and over a considerable length (many tens of kilometers) of the channel.

Background alluvium is usually variously grained (generally medium- and fine-grained) sand with gravel and pebble inclusions and a low content of the silt and clay fractions; it is also characterized by relatively good sorting. The share of sand fractions in alluvium reaches 80–95%; clay particles, 0.6–3%. Technogenic silts (from the grain size aspect) are described as sandy or fine-grained silty (sometimes coarse-grained silty) silts, characterized by poor sorting. The share of sand fractions in silts decreases to 40–60%; the silt fractions increase to 25–50%; and clay, to 8–26%. The main morphometric characteristics and indicators (median diameter, mean diameter, sorting coefficient, asymmetry coefficient, and clay content) of silts differ sharply from background alluvium. Whereas the average (median) size of alluvium particles varies, as a rule, in from 0.1 to 0.2 mm, the average (median) size of particles making up silts is 0.015–0.078 mm. A characteristic feature of the grain size distribution of silts is a sharp increase in the number of particles corresponding to the silt-and-clay fraction, up to 10–31% (vs. 1–3.5% for background alluvium). This largely determines the most important physical properties of silts (their plasticity, stickiness, cohesion, and moisture- and chemical-retention ability). The grain size distribution of silts reflects the composition of SS generated at city treatment plants, the main source of technogenic sedimentary material in rivers of urban and industrial–urbanized areas. With distance from the source of pollution, silts show a decrease in the content of fine fractions (silt and clay) and enrichment of lower layers in sand particles, which results from differentiation of sediment transported by the water flow and its redeposition. From the geological–engineering point of view, background alluvium pertains to loose soils; silts are usually cohesive soils. Differing by a high amount of silt-and-clay particles and organic matter, silts are highly erosion-resistant, make up various forms of the channel relief, and affect the channel dynamics and the course of the channel process.

The mineral composition of background alluvium is close to the composition of the parent rocks and terrigenous-mineral provinces. The influence of other factors occurs against a background of qualitative and quantitative sets of minerals, which are determined by the parent rocks. Usually in natural conditions within a single supply province, there are no sharp spatial changes in the mineral composition of channel alluvium. The observed variations in qualitative and quantitative composition are insignificant and cause no fundamental change to the mineral associations characteristic of a given river (basin). In areas of technogenic pollution, the main changes in mineral composition of the channel sediments of lowland rivers are manifested as a change in the quantitative ratios of minerals that associate with one another in natural background alluvium conditions. The degree of this change significantly increases with increasing technogenic impact (in the sequence background–agricultural area–city–landfill). This is due to an increase in the rates and volumes of technogenic sedimentary material input into watercourses, as well as the unique environmental conditions of technogenic sedimentation. In the light fraction of silts, a directional decrease in the content of the main rock-forming minerals is recorded—quartz and feldspar, altered minerals, rock fragments, and microcline (marked carbonate minerals, limonitized fragments)—as well as a significant increase in authigenic glauconite and acid (Na–Ca) plagioclase, the occurrence of chlorite, muscovite, chalcedony fragments, and volcanic basic and acid glass. In the heavy fraction, there is a significant increase in the content of iron hydroxides and a significant decrease in epidote. There is also a directional increase in the total amount of minerals with pronounced magnetic susceptibility. Silts contain such minerals as portlandite, mullite, pyrite–marcasite, apatite, and kyanite typical of various types of waste and emissions. The content of clay minerals in silts reaches 0.2–3.4% (in background alluvium, it is less than 0.1%). Silts differ by a higher content of accessory minerals that are stable in the hypergenesis zone, such as staurolite, kyanite, rutile, anatase, and tourmaline (total 18–21% vs. 14% in background alluvium), which is reflected in an increased stability coefficient (from 0.6 to 1.5–2). Silts show a significant decrease in the share of minerals with low hydrodynamic stability (from 48 to 22–32%) and low migration ability (from 5 to 3%). Silts are characterized by a significant amount of amorphous matter (up to 30% or more; in the background alluvium it does not exceed 11%). The amorphous matter in silts plays an important geochemical role, significantly increasing their colloidal activity, swelling capacity, stickiness, and hydrophilicity. Whereas background alluvium is characterized by moderate chemical maturity, technogenic silts are characterized by low chemical maturity. A certain role in the formation of the morphological appearance and material composition of river sediments in technogenic pollution areas is played by artificial materials and particles entering watercourses with surface runoff, water runoff, and waste. In exceptional cases, sediments are formed in the channels of polluted rivers that will eventually develop into unique technogenic sedimentary rocks. Mineralogical features of silts determine the uniqueness of their chemical composition and their high content of amorphous matter, carbonate minerals, iron hydroxides, other new formations, and authigenic and clay minerals predetermine the potential secondary transformations of silts and the behavior of associated chemical elements.

Background alluvium, which has been in metastable conditions of the oxidation zone for a long time, is distinguished by a higher degree of differentiation. The petrochemical composition of alluvium is naturally close to that of the sediments and soils making up the catchment basins, which is manifested in the dominance of SiO_2 (75–82%) and Al_2O_3 (4.5–11.5%). Technogenic silts are immature formations, the duration of their formation (from the geological aspect) is short; they are distinguished by a low degree of differentiation and ability toward active diagenetic alterations in their host material. The petrochemical composition of silts is very peculiar and close to that of urban SS (which is a geochemical analog of technogenic silts). The SiO_2 content in silts frequently decreases to 42–62%, the amount of organic matter increases significantly (the LOI values of silts are 10–26% or more vs. 1.67–3.60% in background channel alluvium) and CaO (from 0.8–3.6% in background alluvium to 6–10% or more in silts). Silts differ stably by increased contents of iron, titanium, and sulfur compounds.

The group composition of organic matter in the background alluvium of lowland rivers is close to that of organic matter in sedimentary rocks and especially soils that form the catchment area, since it is mainly determined by the mechanical differentiation of incoming allochthonous sedimentary material and, to a much lesser extent, by the accumulation of autochthonous organic matter. This results in a low content of organic matter (C_{org} = 0.65%) in alluvium and the prevalence of humic acids in its composition (81.8% of C_{org}) with an insignificant share of residual organic matter (16.7%) and lipids (1.5%). Alluvium is characterized by a fulvate–humate type of organic matter and a very high degree of humification, which points to predominant oxidative processes under natural conditions. Technogenic silts have a higher organic matter content (C_{org} 1.26–2.60%); the sharpest increase is observed in the specific concentrations of lipids (6–59 times compared with background alluvium) and insoluble organic matter (3–11 times). To a significantly lesser extent (by 1.3–1.6 times), the specific content of humic acids, which are already dominated by fulvic acids, increases in silts. Silts differ from alluvium by a different structure of the group composition of organic matter in them: the relative share of lipids increases to 10–20%, residual organic matter increases to 27–48%, and the share of humic acids decreases to 29–57%. Near a source of pollution, organic matter in silts is characterized by a medium and high degree of humification and a fulvate–humate type of humus, which indicates predominant reduction processes. With distance from a city, the total organic matter content in silts decreases mainly due to a decrease in the amount of humic acids and poorly soluble organic compounds. In silts, the amount of organic carbon significantly exceeds the carbonate carbon content, which distinguishes them from alluvium and other sedimentary formations. Petroleum products play an important role in the formation of the physical properties, texture, and structure of silts, their color, and odor: the contents of petroleum products can reach several hundred mg/kg or more. The organic matter that concentrates in silts largely determines their physicochemical properties and plays an important role in the behavior of heavy metals.

All types of industrial production determine the formation of technogenic geochemical anomalies in sediments (especially in technogenic silts) in rivers that receive wastewater and surface runoff from developed territories. The impact of various industrial–urbanized facilities on watercourses is reflected by silt accumulation in a qualitatively similar geochemical association. Hg, Ag, Cd, Co, Cu, Ba, Zn, Cr, P, Sc, and Sr are encountered nearly everywhere. Chalcophile elements (possessing high toxicity) are distinguished by the highest K_C values. The qualitative and quantitative parameters of pollution of watercourses (of approximately equal orders) depend more on the industrial infrastructure of settlements rather than their size. The heaviest and most compositionally complex geochemical anomalies are typical of enterprises (industrial zones) that use physical and chemical processes in the process cycle, production and processing of nonferrous metals, etc. The geochemical specialization of enterprises and industrial zones is manifested mainly in different intensities of chemical element concentration in silts; to a lesser extent, in the occurrence of elements characteristic only of a particular facility.

Bottom sediments (and especially technogenic silts) in which extensive (tens of kilometers) multielement geochemical anomalies (technogenic dispersed flows) are formed reflect the most completely the parameters and morphology of zones of influence of various sources of river pollution. The spatial features of the chemical element distribution in silts are due to the geologically insignificant formation time of the latter, the discrete nature of pollutants entering watercourses, natural channel differentiation of sedimentary material, the lithological–geomorphological features of river channels, and the properties and stratification of silts. The most important feature of the chemical element distribution in technogenic silts is significant spatial variation of their concentrations both vertically in the sediment sequence and laterally downstream. For most chemical elements, this variation (nonuniform distribution) is usually manifested against a background of their high concentrations. The degree of spatial separation of geochemical associations in silts is small, and the chemical element distribution usually has a high degree of consistency. Natural differentiation and the specifics of sediment accumulation in river channels, which are a naturally constructed morphological complex complicated by natural and artificial geochemical barriers, results in an inhomogeneous (variegated) areal structure of geochemical anomalies in the bottom sediments of watercourses. The natural character of the spatial chemical element distribution in channel sediments can be complex at geochemical barriers, the existence of which is due to changes in the geomorphological features of the river channel and valley, from both natural and artificial causes.

The chemical element distribution in the grain size distribution of background channel alluvium is characterized by their increased specific concentrations from coarse to finer fractions. A similar distribution pattern of the majority of the studied chemical elements (but with their higher specific contents in specific fractions) is also observed in silts. The exceptions are Fe (the main concentrator of which is the coarse-grained silt fraction) and Hg (the concentrator fraction is fine- or medium-grained sand), which is due to the characteristics of the structural-aggregate composition of silts. For the majority of metals, coarse-grained silt acts as the carrier fraction, with which up to 50–70% of their total content is associated. For mercury, the main carrier in silts are the medium- or fine-grained sand fractions (near the source of pollution) and fine-grained sand or silt fractions (with distance from the source of pollution).

The technogenic silts that form in channels of lowland rivers in pollution zones differ from the background channel alluvium by a different ratio of the main mineralogical and geochemical forms of heavy metals. This is manifested as a marked increase in the share of their mobile compounds capable of passing into the aqueous phase and being taken up by hydrobionts. The specific concentrations of the mobile forms of many metals in silts are not only close to the gross background contents, but often exceed them. The forms of heavy metals and, especially, their ratio in technogenic silts near pollution sources are usually close to the species and their ratio in sedimentary material (technogenic SPM) transported to rivers with wastewater, which indicates the importance of hydraulic (mechanical) processes in the formation of these silts in technogenic SPM deposition areas. With distance from the source of pollution, sorption processes play an important role in the precipitation of heavy metals transported by the water flow. Usually, downstream, there is a decrease in the relative share of forms of heavy metals with low mobility, and the balance (ratio) of their main forms approaches that in background alluvium. Nevertheless, in most cases, the potential reserve of metals capable of further transformation and assimilation by aquatic organisms in silts exceeds the total pool of chemical elements in background channel sediments. Silt water in technogenic pollution zones is characterized by high concentrations of chemical elements and compounds thereof (significantly higher than their levels in bottom water and background concentrations in river water). This points to a constant directional concentration gradient of dissolved forms of pollutants from sediments to water at the water–silt boundary. A direct dependence has been established for mercury content in silt water on the concentration of this metal in silts.

Technogenic silts (in comparison with background alluvium) are characterized by higher dry residue values, high exchange acidity, and significant contents of exchangeable ions. Whereas the cationic exchange capacity of background alluvium is 4.84 mg-eq/100 g of sediment, in silts it increases significantly, reaching maximum values of 38–41 mg-eq/100 g. Silts with the lowest pH values demonstrate the highest cation exchange capacity. Calcium dominates in the composition of exchangeable cations (68–81% of the total); the share of exchangeable magnesium is also significant (32–36%). The amount of exchangeable NH_4^+ significantly exceeds the content of exchangeable sodium and potassium. Silts is also characterized by elevated NO_3^- contents.

Secondary silt transformations may be associated with the transformation of organic, carbonate, and silt-and-clay components; the transformation of iron compounds and the formation of “fresh” iron, manganese, and aluminum hydroxides and their hydrosols; secondary aluminosilicates and amorphous minerals—with the transition of amorphous iron hydroxides, manganese, and aluminum into crystalline forms, with silts losing unbound water as they compact, with a relative increase in the content of stable titanium minerals, and, to a significant extent, with blending of technogenic material and natural alluvium. The breakdown of organic matter, which is present in significant quantities in technogenic silts, may intensify gas formation processes, facilitating the entry of certain pollutants from sediments into the main water flow.

In the long-term, technogenic silts are a powerful source of secondary pollution of the water mass and floodplain areas and hydrobiont uptake of toxic substances, the impact of which occurs through a variety of physicochemical, biochemical, and hydrodynamic processes occurring in river systems, including directly in sediments and at the bottom water–silt boundary.

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