Assesement of groundwater and unsaturated zone contamination in urban areas

I. GALITSKAYA, I. POZDNYAKOVA

Hydrogeology, Institute of Environmental Geosciences Russian Academy of Science, Russia (gal@geoenv.ru)

Abstract: At the present time, there is no unified approach for assessing the geochemical risk to the population resulting from contaminated vadoze zone soils. Overestimation of the risk leads to excavation and the removal of excessively large volume of soils. Assessment of the role of unsaturated zone soils as a secondary source of contamination could be one approach to risk estimation. The main criteria in this approach are the travel time of contaminants to groundwater level, concentration of species in soil water and the level of complex pollution. The main method of risk calculation in this approach is based on vadoze zone flow and transport modeling. This approach was applied to two urban sites in the Moscow metropolitan area. The first site is a site of an unauthorized surface waste dump. The second site is an area of park ponds within a recreation zone. It was found that heavy metals, nitrogen species, oil and PAH pollutants contaminate topsoils, the unsaturated zone and groundwater. Estimated by traditional approach of excavation, the depth of contamination in the soil reached to a depth of 15 m. In our approach unsaturated flow and transport modeling was performed with WHI UnSat Suite Plus. Modeling of contamination showed that unsaturated zone at these sites will be the secondary source of contamination for up to a hundred years. Due to low recharge to wash out pollutants, the rate of mass loading on groundwater level is low. Thus, mixing of contaminated recharge and natural groundwater does not increase the concentration in groundwater over the maximum allowed value. These results allow us to develop alternatives to excavation methods of remediation for these sites. Sensitivity analysis has shown that the sorption parameter has a serious effect on contamination. These parameters can change vertically and spatially within the investigated sites. Thus, to develop a remediation solution, the sorption of different species has to be studied during the site characterization stage.

Résumé: Le problème essentiel sur les territoires urbains est la restitution du milieu pollués naturel. La méthode commune, permettant estimer le danger géochimique pour la personne des sols pollués et les races de la zone de l'aération, à présent manque. L'estimation du rôle des sols pollués et les races de la zone de l'aération comme de la source secondaire de la pollution de l'eau souterraine peut être un des approches de l'estimation du danger de tels objets. L'utilisation des comptes transport des substances polluant dans la zone de l'aération est la méthode principale de la décision de telles tâches.Cette approche est appliquée à Moscou pour le territoire du dépôtoir non sanctionnés et la zone de parc du repos. Les sols, la race de la zone de l'aération et l'eau souterraine sont pollués par les métaux lourds, les liaisons de l'azote, les produits pétroliers sur ces territoires. La profondeur maxima de la saisie des races polluées pour les estimations traditionnelles sur les terrains particuliers faisait jusqu'à 15 m. Les comptes de la migration étaient faits à l'aide de l'ensemble de programme WHI UnSat Suite Plus la (version 2.2.0.2). Les comptes ont montré que n'importe quelles variantes de la saisie des races polluées la zone de l'aération au cours de quelques centaines ans restera la source de l'entrée des substances polluant à l'eau souterraine. Cependant la concentration des substances polluant dans l'eau souterraine sous le foyer de la pollution peut rester dans la limite de la norme. Les résultats permettent de proposer les moyens alternatifs de la restitution du territoire. Par les paramètres principaux influençant l'exactitude des décisions de pronostique, sont les paramètres de l'adsorption. Ils peuvent beaucoup changer selon la coupe. Les expériences de laboratoire sont nécessaires à l'argumentation des décisions de pronostique par la définition des paramètres de l'adsorption.

Keywords: excavation, numerical models, pollution, soils, unsaturated zone, urban geosciences.

INTRODUCTION

One of the major problems at transition of a society to sustainable development is ecological safety of the population in cities (megacities in particular). The assessment of human health risk from the geochemical hazard caused by contamination of environment abiotic components has special value at formation of the city environment under the conditions of constantly worsening ecological conditions. The most urgent task in the urbanized territories is the geochemical hazard assessment of the topsoil and vadoze zone soils. It is necessary to take into account not only hazard for the population of contaminated topsoil dispersion, but the hazard of contaminated vadoze zone soils for ground and surface waters too.

At the present time in Russia, there is no unified approach for assessing the geochemical hazard resulting from contaminated vadoze zone soils. The assessment of soil hazard as secondary contaminant source for ground and surface waters is standardised only for heavy metals. In this case a migration water parameter is used. Pollution of waters occurs if concentration of an element in soils is higher than a migration water parameter value. In this approach the mineralogical structure, adsorption - desorption parameters and unsaturated flow and transport parameters are not taken into account.

Categories of hazard determined on size of factor of concentration K (K – is a relation of the element content in soil to the migration water parameter) scientifically are not proved. Overestimation of the hazard leads to excavation and the removal of excessively large volume of soils. Approaches to the optimum decision of secondary contamination source liquidation problem in vadoze zone soils was applied to representative urban sites in the Moscow metropolitan area. The first site is a site of an unauthorized surface waste dump. The second site is an area of park ponds within a recreation zone.

THE ESTIMATION OF THE OPTIMUM EXCAVATION CONTAMINATED SOILS DEPTH AT THE NOT AUTHORIZED SURFACE WASTE DUMP

The study area is located on the land of former filtration fields. The utilization of sewage was begun since 1914.

The removal of the sewage sludge and filling up different sites of this land by soils were begun in 1980. Then these sites were used for house-building. The sewage sludge from the study area was partly removal and the non-authorized dump was formed on the fill soils (Figure 1).

Figure 1. The study area

The size of this site is 94000 m² about. More than 40 wells were drilled for investigation of geology, engineering geology and hydrogeology conditions of the site. Well drilling was accompanied by soil and groundwater sampling for the chemical analysis. Data analysis showed that the fill soils contain the impurities of building dust and household waste (Figure 2).

Figure 2. The fill soils

The soils over unsaturated profile including fill soils, sewage sludge and underlying soils are contaminated by heavy metals. The concentrations of all chemical elements in the soils widely vary from low to high values (Table 1).

Table 1.

No of the well	Depth of sampling (m)	Concentration of chemical elements, mg / kg											
		Pb	Cd	Cu	Zn	Ni	Co	Mo	Mn	Sb	Cr	Hg	As
300	1.0	123.0	0.62	69.2	80.6	115.2	2.36	0.101	366.9	0.7	45.8	0.0770	0.63
	3.0	84.6	0.71	54.6	136.5	32.3	3.17	0.040	324.7	0.9	62.4	0.0450	0.44
	3.5	80.2	1.25	59.5	36.7	57.9	0,59	0.080	954,8	0.8	62.4	0.0030	<0.1
	6.0	75.,7	0.93	47,9	62.8	48.3	2.54	0.079	542.6	0.8	43.7	0.0044	<0.1
	1.5	67.4	1.24	23.4	58.9	27.1	0.43	0.014	404.7	0.7	54.1	0.0968	<0.1
344	0-0.5	98.5	3.16	1057.3	547.8	746.2	10.72	2.039	7727.4	2.0	102.10	0.4640	2.7
	4.00	4480.0	10.94	2981.7	950.4	257.8	7.85	2.825	1056.0	0.6	93.70	0.0570	0.4
	7.00	728.5	7.27	133.3	713.9	144.2	2.24	0.685	2815.6	1.6	68.80	0.0410	1.9
	7.80	331.0	4.34	94.9	115.7	97.4	2.17	1.400	970.4	2.2	45.0	0.0740	0.7
	15.00	202.0	0.42	72.7	129.7	52.6	1.02	0.277	262.7	0.3	59.3	1.1630	0.5

The total concentrations of heavy metals and the concentrations of heavy metal mobile forms in mg/kg are shown in Figure 3. The concentrations of some metals like nickel (Ni) and cobalt (Co) decrease with depth. The concentrations of other metals like lead (Pb), cadmium (Cd), copper (Cu) and zinc (Zn) increase to depth of 4 m and then decrease.

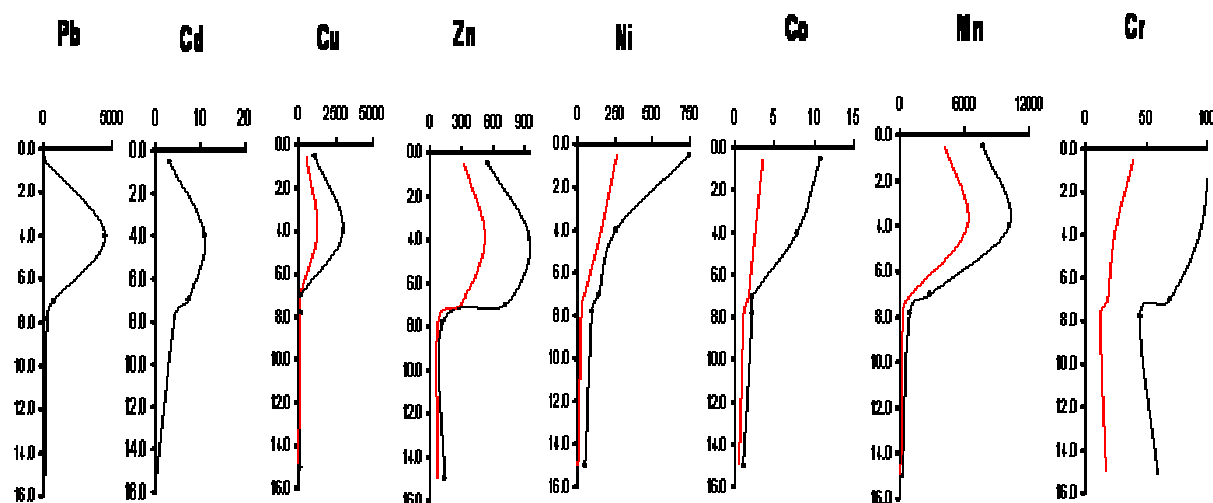The maximum concentrations of such elements were found in the sewage sludge layer.

Figure 3. The heavy metals distribution in the unsaturated soil profile to a depth of 15 m (well 344); black lines indicate the total concentrations, red lines indicate mobile forms concentrations.

The generalized type of contaminant association against the background is:

$$Pb_{172}\,Hg_{129}\,Cu_{110}\,Ni_{37}\,Cd_{36}\,Zn_{22}\,Mo_8\,Mn_6\,Cr_5\,Sb_4$$
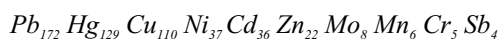
where the index to the right of a chemical element symbol is the maximal size of factor of K. K is the relation of element concentration to a background.

$$Hg_{21}\,Pb_{10}\,Cu_8\,Cd_5\,(Ni,\,Zn)_4\,Sb_2$$
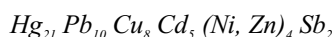
where the index to the right of a chemical element symbol is the average value of K.

The most significant excess of maximum allowed value are found for lead (up to 140 maximum allowed value), copper (up to 90.4 maximum allowed value), zinc (up to 21 maximum allowed value), nickel (up to 37.3 maximum allowed value), cadmium (up to 21.9 maximum allowed value). The average percentage of mobile element forms (available for adsorption forms) from their total contents is: 40 % for copper, - 44 % for zinc, - 30 % for nickel, 50 % for manganese, –up to 89 % for cobalt, 32 % for chromium. Significant percentages of mobile forms are caused by their high adsorption ability.

The assessment of the vadose zone soil hazard as the contamination secondary source of ground waters was a necessary stage at an assessment of an ecological territory condition. This assessment is performed by comparison of copper mobile form concentration (as one of the basic contaminant) with migration water parameter value. Very high

(K > 30) and high (10 < K < 30) categories of soil contamination were determined in fill soils and sewage sludge layer on separate sites (K - factor of concentration concerning a migration water parameter). Alluvial soils were characterized by average (3 < K < 10) or low (1 < K < 3) categories of soil pollution. The categories of soil contamination scientifically are not proved, and the given approach does not allow improving the estimate of optimum depth of contaminant soil excavation. That is why the numerical analyses of unsaturated flow and contaminant transport were used for developing scientific criteria of contaminated soils hazard estimate and for developing alternative approach to estimate depth of contaminant soil excavation and remediation this site.

Vadoze zone flow and transport modeling

Typical unsaturated profile conditions. It is possible to allocate two basic types of vadoze zone profile conditions in investigated territory by results of drilling. The first type is specific for sites where sewage sludge was kept in vadoze zone after remediation (Figure 4).
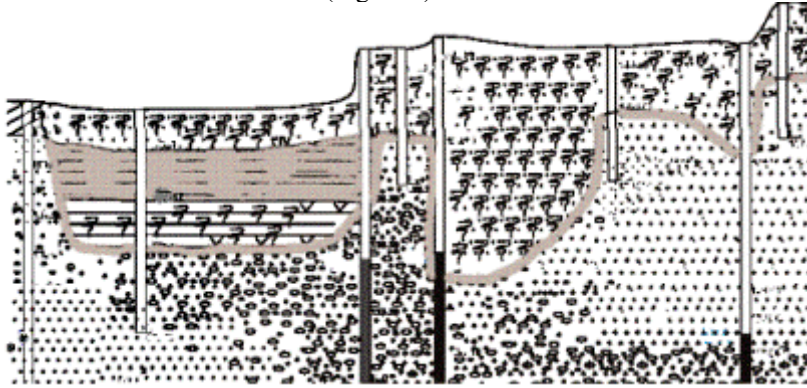

Figure 4. The first type of vadoze profile conditions

At these sites the top part of "fill soils layer" approximately up to 1.5 m consists of fine and coarse sand with impurity of building dust - gravel, rubble, fragments of concrete, a crumb of a brick, wood chips, splinters of glass. The bottom part of "fill soils layer" in the interval from 1.5 m up to 4 m is presented by sand with interlaying of turf, loam and clay. This part contains impurity of decaying domestic waste - rags, a cardboard, a paper, polythene, plastic, rubber. The "sewage sludge layer" consists of black clay layers with impurity of excrements and lies more deeply 4 m. The thickness of this layer changes from 0.7 m up to 3 - 4 m. Fill soils and alluvial heterogeneous sand underlie the sewage sludge layer. The total thickness of underlying soils is equal to 2 m - 7 m. The water table is 9 - 15 m deep in places where the first type of vadoze profile conditions is occurred. The amount of copper mobile forms in the soil solid phase averaged by the profile is more than 30 mg/kg (or 10 maximum allowed values). Maximum amount of copper mobile forms 1200 mg/kg (or 400 maximum allowed values) was found in the "sewage sludge layer".

The second type of vadoze profile conditions is presented in places near or between sewage tanks. The profile of vadoze zone consists of the top part of the "fill soils" and alluvial heterogeneous sand layer. The "fill soils" is presented only by sand including the building dust. The thickness of the "fill soils" decreases to 1.5 m in some places. The water table is 5 - 11 m deep. The amount of copper mobile forms in the soil solid phase averaged by the profile dos not exceeds 10-20 maximum allowed values in most cases. The highest concentration of copper mobile forms found in the soil does not exceed 100 maximum allowed values.

The comparison of two types of vadoze profile indicates there are significant differences between unsaturated profile conditions. At those sites, where vadoze zone profile contains "sewage sludge layer", the profile conditions are characterized by heterogeneous structure, maximum "fill soils layer" thickness and copper content in the soil. Besides, penetration of the highest copper concentration into the soil is the deepest.

One-dimensional flow and transport modeling through the unsaturated zone was performed under following conditions. It was supposed that soil contamination was formed during long time period of 40 - 100 years as a result of copper inflow with groundwater recharge. Groundwater recharge rate was accepted constant and equal average annual rate over 100 years. Concentration of copper in recharge was accepted constant and equal to the copper concentration in liquid phase of sewage sludge - 1000 mg/l. Homogeneous lithologic layers were divided into modeling layers according to amount of selected samples. Copper concentration in soil solid phase was constant through each modeling layer. Also it was supposed, that copper migrates in the form of simple cation. Transport of copper with a moisture and adsorption by soil are the main processes responsible to distribution of copper through the soil profile. Data required to unsaturated flow and transport modeling were taken from available databases.

The unsaturated flow and transport modeling was performed with WHI UnSat Suite Plus package [1]. This package includes models designed for simulating one-dimensional unsaturated flow. HELP and VS2DT models were used to estimate groundwater recharge rates and travel time of contaminant to groundwater level.

Estimate of groundwater recharge rates

At the first stage the HELP program was used to estimate average annual groundwater recharge rate over 100 years. The HELP model is a quasi-two-dimensional, deterministic, not very complicated water-routing model for determining water balances [3]. HELP uses numerical solution techniques that account for effect of surface storage, snowmelt, runoff, infiltration, evapotranspiration, vegetable growth, soil moisture storage, lateral subsurface drainage,

unsaturated vertical drainage or leakage through soil. Data required for modeling include weather data (daily values of precipitation, air temperature and solar radiation), soil data (porosity, field capacity, wilting point, hydraulic conductivity) and engineering design data (surface slope, runoff collection system e.t.c.). Data representing meteorological conditions can be specified or stochastically generated by Weather Generator. Daily values of precipitation, air temperature and solar radiation for 100 years period were generated by Weather Generator using average monthly atmospheric precipitation and temperature data observed by Moscow observation during 1945 - 1995 years period. Soil properties data for modeling layers were assigned using default values from database (Table 2.). Average annual groundwater recharge rate estimated over 100 years is 158 mm/years or 0.0004 m/day.

Estimate of copper distribution coefficient

At the second stage the copper distribution coefficient (K_d) between solid and liquid phases of soil was estimated. For this modeling copper concentrations obtained by ammonium acetate extracts from soil samples were applied. The copper concentrations in a mobile form were supposed to be equal ion copper concentrations in ion exchange and adsorption complex of soil. The VS2DT program allows simulating unsaturated vertical flow based on solution of Richardson equation [2] and modeling contaminant transport with adsorption. For the solution of Richards' equation, van Genuchten soil hydraulic function were used. Adsorption and desorption processes were described by linear Henry isotherm.

The initial water conditions included equilibrium distribution of moisture in the profile. Constant recharge rate 158 mm/year was specified at the upper flow boundary. Pressure head equal zero was specified at the lower flow boundary.

Table 2. Modeling layers property

Layer name	Modeling material category	Modeling layers property			
		Total porosity	Field capacity	Wilting point	Saturated hydraulic conductivity (m/day)
fill soil	domestic waste	0.67	0.292	0.292	0.86
sewage sludge	loam	0.45	0.232	0.116.	0.25

Initial chemical distributions included copper concentrations in soils accepted equal to zero. Copper concentration equal 1000 mg/l was specified at the upper transport boundary. Thickness of modeling unsaturated profile was accepted 8.7 m. The VS2DT program uses the finite element method to approximate the unsaturated flow and transport. The modeling unsaturated profile was divided into cells of 0.1 m step length. Values of parameters of dispersion, molecular diffusion, bulk density were accepted for all types of soils by default from a database included in UnSat Suite Plus. These parameters were accepted for "fill soils" layer according to 0.45 m, 0.47 sm^2/day, 1.4 g/sm^3; for "sewage sludge" layer - 0.7 m, 0.2 sm^2/day, 1.4 g/sm^3 appropriately.

The matching of copper distribution coefficient between solid and liquid phases of soil was obtained in this way for each layer. Copper concentrations in liquid phase obtained by modeling were calculated using Henry equation in solid phase copper concentrations. Then these copper concentrations were compared to observed concentrations in the solid phase. The matching of copper distribution coefficient was produced for two different possibilities of copper profile generation. It was supposed that the copper concentration profile was formed during the 40-ty years period in the first series of variants. The modeling time was 40 years and the copper distribution coefficient was matched for each layer. In the second series of variants the modeling time was 100 years. It was supposed that copper concentrations in the "fill soils" layer were formed as a result of washing out pollutants from waste dump. The copper distribution coefficient was estimated only for "sewage sludge" layer and underlying layer in these variants. The copper distribution coefficient matching results are applied in the Table 3.

Table 3. The copper distribution coefficient matching results

Layer number	Layer name	Layer thickness (m)	Deep of sampling (m)	Observed copper concentration in solid phase (mg/kg)	Modelled copper concentration		
					in liquid phase (mg/l)	K_d (ml/g)	in solid phase (mg/kg)
1	"fill soil"	1.5	0.5	496	995	0.5	497
2	"fill soil"	2.5	2.0	500	997	0.5	499
3	"sewage sludge"	0.7	4	1270	858 488*	1.5 2.5*	1280 1220*
4	"fill soil"	2.3	7	74.8	716 52*	0.1 2*	72 104*
5	"fill soil"	0.7	7.8	55	665 26*	0.9 2*	59 52*
6	"fill soil"	0.9	8.7	30	635 17*	0.05 2*	31 34*

* Values in second series of variants

Comparison of modeling results shows that values of copper distribution coefficient for layer 3 of sewage sludge obtained in both series of variants are close. Values of copper distribution coefficient for underlying layers differ in 20 - 40 times. The obtained modeling results do not allow making a certain choice of copper distribution coefficient values. Lower and high values of copper distribution coefficient correspond to experimental data. For the further estimates of copper travel time to groundwater level the both series of variants of copper distribution coefficient values were used.

Estimate of the copper travel time to groundwater level

At the third stage modeling unsaturated flow and transport was used for estimate the time of complete copper washing out from soil as a result of clear precipitations infiltration. Besides it was estimated the time after that the copper concentration in solid phase decreases to allowed values - 72 mg/l. The copper concentration in groundwater recharge was accepted equal to zero, initial copper concentration in liquid soils phase in the profile conformed to the copper concentration in solid phase of soils in observed points.

Copper travel time estimates were performed for several variants of soils excavation: no soils excavation (variants 1.1, 2.1); soil excavation of upper layers 1 and 2 (variants 1.2, 2.2); soil excavation includes the most contaminated layer 3 (variant 1.3). The excavation and replacement of contaminated soils by uncontaminated soils were realized by specifying initial copper concentration in soils equal to zero for modeling layers.

The modeling results

The complete copper washing out from soil as a result of clear precipitations infiltration occurs up to a hundred years in variant 1.1 with low values of copper distribution coefficient. Decrease of copper concentration in solid phase to values corresponding with allowed copper values in liquid phase - 72 mg/l in whole unsaturated profile occurs in fifty years in this variant.
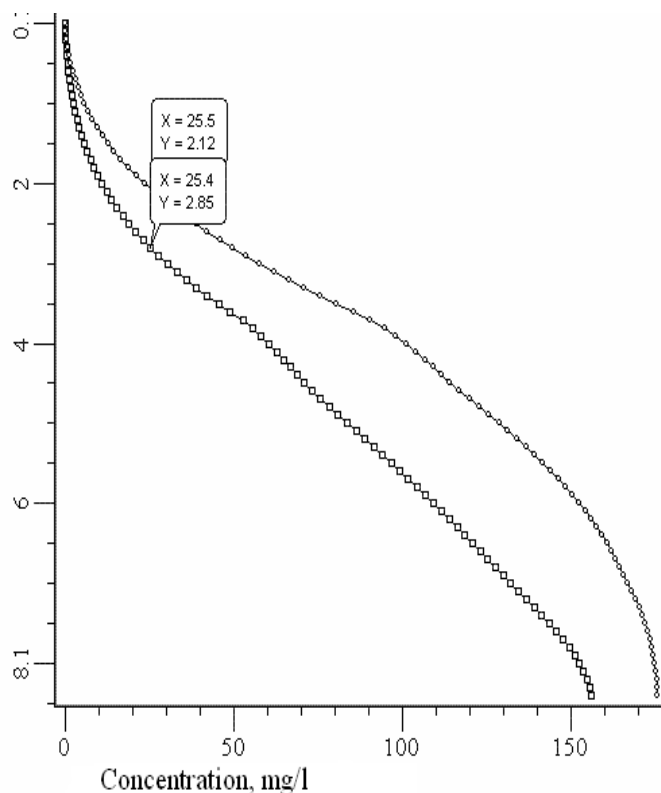
○ – 100 years, □ – 130 years

Figure 5. The copper concentration in liquid soil phase in the unsaturated soil profile to a depth of 8.7 m (variant 2.1)

The complete copper washing out from soil as a result of clear precipitations infiltration does not occur even up to a one hundred and thirty years in variant 2.1 with higher values of copper distribution coefficient. Decrease of copper concentration in soil to allowed values - 72 mg/l occurs only to a depth of 2.85 m during this time period (Figure 5).

The complete copper washing out from soil as a result of clear precipitations infiltration occurs up to ninety years in variant 1.2 with soil excavation of upper 1 and 2 layers and low values of copper distribution coefficient. Decrease of copper concentration in soil to allowed values - 72 mg/l in whole unsaturated profile occurs in forty years in this variant. The complete copper washing out from soil as a result of clear precipitations infiltration occur up to seventy years in variant 2.3 with excavation of contaminated soils including layer 3 and with higher values of copper distribution coefficient. Decrease of copper concentration in soil to allowed values - 72 mg/l in whole unsaturated profile occurs in twelve years in this variant.

Thus the modeling of unsaturated flow and contamination showed that the complete copper washing out from soil happens during long time period of a hundred years in all modeling variants. Decrease of copper concentration in soil to allowed values - 72 mg/l in whole unsaturated profile occurs most quickly after excavation sewage silt deposits.

THE ESTIMATION OF THE OPTIMUM EXCAVATION CONTAMINATED SOILS DEPTH AT THE RECREATION ZONE AREA

The problem of environment oil product contamination in Lefortovo Park has occurred at remediation work of the cascade of the Park ponds. These ponds had a natural recharge due to groundwater discharge. Pond water and bottom sediment contamination by oil products was found during the previous investigations.

It was supposed to clean the ponds through remediation works in the park. One of the primary goals was maintenance of pondswater quality. For a substantiation of prevention actions of pond pollution there was a need to study the contamination conditions including possible inflow sources, ways of migration of contaminants, the impact of contaminated ponds water on the Lefortovo Park environment.

It is necessary to notice, that oil products refer to 4 classes of hazard, however the hazard estimated for different component oil products such as aromatic hydrocarbons can be higher. Aromatic hydrocarbons (benzene, toluene, xylene etc.) and the polycyclic aromatic hydrocarbons (PAH) refer to the most toxic hydrocarbon components of oil product. PAH have carcinogenic, mutagenic and other toxic properties in relation to living organisms. Benzo(a)pyrene is the strongest carcinogenic and mutagenic among PAH compounds. Toxicity of oil products is believed can not be determined by separate estimate component toxicity, it is necessary to account for the influence of a complex of the substances as a whole. This problem is insufficiently developed, that is why the most widespread approach is the risk assessment for human health of the most toxic components considered individually.
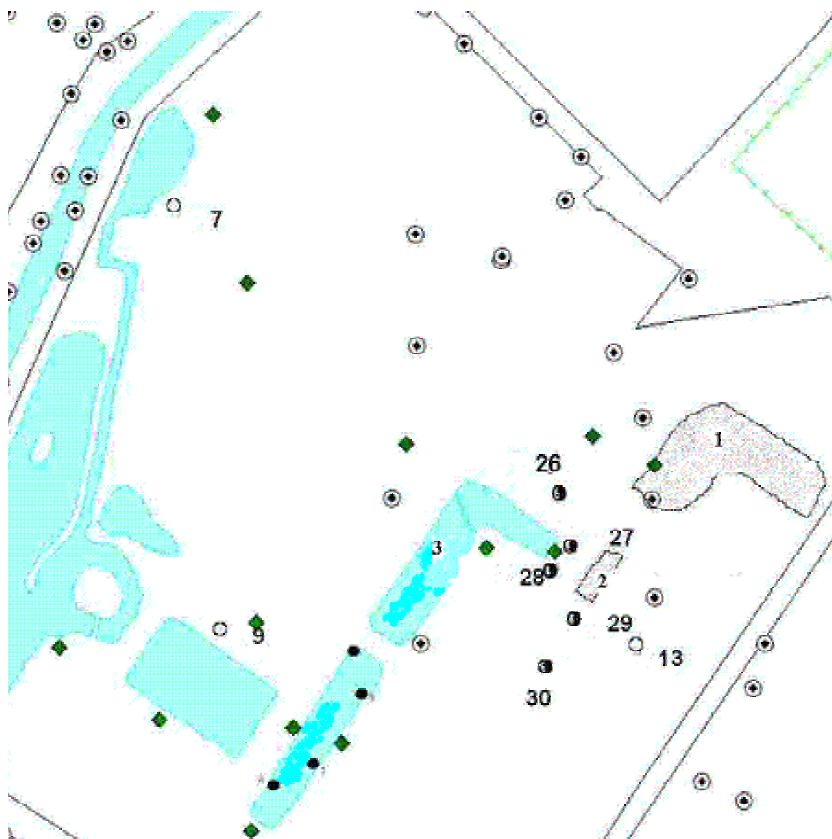
Figure 6. Lefortovo Park recreation territory 1 – garages; 2 - gasoline storage; 3 – Ponds; 26-30 – the points of soils and groundwater sampling, ▌ - the points of snow sampling; ● - the points of bottom deposits sampling.

The potential sources of oil products in Lefortovo Park are located in a recharge zone of ponds above a slope (Figure 6). These are the garages, gasoline storage, underground non-combustive-lubricating storage, and the car wash nearest to the Park. Motor transport can be the source of oil product (benzene, toluene) and PAH. There is a high probability of vadose zone, groundwater and seasonal stream contamination and as a result pond water and bottom deposit contamination. Field investigations and laboratory analyses were performed to identify the sources of oil product and individual PAH contamination.

The contamination of groundwater by oil products was found only in the 26-29 wells. The water table is 6.1-6.5 m deep. The highest concentrations of oil product were found in groundwater samples obtained from 26 well were 18.6 mg/l. There was a strong petroleum smell, very high turbidity 286-585 mg/l and contents of the weighed substances 131 - 184 mg/l in ground water samples. The oil product concentrations in groundwater samples obtained from wells 27 and 28 were 1.3 and 1.2 mg/l accordingly. The oil products and PAH concentrations in soils samples obtained from wells 26-30 are shown in the Table 4. Data analysis showed that the oil products and PAH concentrations in soils widely spatially vary from low to high values. There were the following oil products contamination conditions of the soil profile: the high contamination level was found basically in the top layer due to high sorption ability of petroleum hydrocarbons especially high-molecular fraction; two high concentrations levels were found at the top of layer and in interval of the depths of 5.0-7.0 m (26 and 28wells). Concentration of oil products in the most contaminated top layer of soils decreased from well 27 (89 maximum allowed values) through well 26 (3 maximum allowed value) to well 28 (0.7 maximum allowed value), well 29 (0.2 maximum allowed value) and well 30 (< 0.03 mg / kg). The maximum allowed value of oil product concentration in soils in Moscow is 300 mg / kg.

Table 4. The concentrations of oil products and PAH in soils

Number of the well	Depth of sampling (m)	Oil products concentration (mg/kg)	PAH concentration (µg/kg)
26	2.0-3.0	902	63000
	3.0-4.0	347	10859
	4.0-5.0	110	4260
	5.0-6.0	325	1968
	6.0-7.0	210	506.1
	7.0-8.0	<0.3	1.1
	8.0-9.0	<0.3	0.94
	9.0-10.0	<0.3	0.74
27	4.0-4.5	26695	56070
	5.5-6.0	22564	38000
	7.3-7.8	12	2.21
28	2.0-3.0	208	396.7
	3.0-4.0	10	2.16
	4.0-5.0	94	3.84
	5.0-6.0	226	2.11
	6.0-7.0	186	6.45
	7.0-8.0	3	1.02
	8.0-9.0	<0.3	0.62
	9.0-10.0	1,0	0.62
29	2.0-3.0	61	51.7
	3.0-4.0	55	62.03
	4.0-5.0	<0.3	0.82
	5.0-6.0	<0.3	0.83
30	2.0-3.0	<0.3	1.42
	3.0-4.0	<0.3	1.31
	4.0-5.0	<0.3	1.3

The maximum concentration of individual PAH were accumulated in the top vadoze zone layer due to of high sorption PAH ability. PAH concentrations for example benzo(a)pyrene concentration in the upper soils layer decreased from well 26 (682.5 maximum allowed values) through well 27 (183.8 maximum allowed values), well 28 (2.3 maximum allowed values) to well 29 (0.05 maximum allowed values) and well 30 (0.002 maximum allowed values).

The types of individual PAH associations can also indicate the origin of soil contamination. Pyrene prevails (27-35 %) in vadose zone soils up to depth of 5.0 m in the most PAH contaminated soils samples obtained from well 26. The type of association changes on depth of 5.0-6.0 m where benzo(a)pyrene becomes the leader (45,7 %). Anthracene takes the first place in association (36-43 %) below the ground water level, other individual PAH's are in the minor position, and the relative benzo(a)pyrene concentration decreased up to 1 %. The type of this association specifies that PAH can proceed by oil products or exhaust gas transport emissions. Taking into account high PAH concentration (63 mg / kg), it is more probable, that PAH are the part of oil products. The depth of soil contamination by RAH depends on RAN mobility. More soluble pyrene and anthracene permeate in vadose zone more deeply than benzo(a)pyrene. Low and approximate equal concentrations of anthracene, pyrene and 11,12 benzfluoranthene in soils (well 30) indicate that RAH can proceed by oil products with infiltration.

Significant vadoze zone soils contamination by oil products and connected with them PAH points to presence of contaminant sources located inside and nearby the recreation area. High contaminant concentrations in groundwater near well 26 can be explained by the inflow contaminated groundwater from northern territory where the garages are located. High concentration of oil products (high-molecular oils mainly) in soils near well 27 can be explained by the inflow from gasoline storage with infiltration. Liquidation of contaminant primary sources will prevent the further environment pollution; however contaminated soil will be a secondary source of contamination for a long time.

Vadoze zone flow and transport modeling

The modeling of unsaturated flow and oil products transport was used to research of contaminated soil and groundwater conditions. The model was produced by using the VLEACH program (1). The main modeling processes were the solution of oil products in a moisture, constant flow and transport of contaminant through the soil, adsorption, diffusion contaminant to atmosphere and leaking to groundwater. The main model limitations included homogeneous structure of soil profile, constant rate recharge, constant moisture, constant contaminant concentration in recharge. The processes of dispersion, biodegradation and volatilization of pollutant were not considered.

The most soluble and toxic forms - benzene and toluene presented the oil products. Values of the main hydrophysical soils characteristics and contaminant properties were specified by default values from database. Groundwater recharge rate estimated previously was 158 mm/year. Oil products distribution coefficient K_d, was calculated using oil products concentration in groundwater and saturated samples (Table 5).

Table 5. Calculation values of oil products distribution coefficient

Well number	Deep of sampling (m)	Oil products concentration		K_d (ml/g)
		in water (mg/l)	in saturated sample (mg/kg)	
26	6-7	18	210	8.3
27	7.3-7.8	1.3	12	6.6
28	6-7	1.2	186	96.8

The modeling included the estimation of oil products contaminated snow on soils contamination and the estimation of the optimum excavation contaminated soils depth. The estimation of oil products contaminated snow on soils contamination was performed for soil profile conditions of the cleanest site near well 29. The results of modeling showed that the benzene concentration in soils would not exceed 2.7-5.2 mg/kg under condition of constant inflow of 39 mm/years due to thawing a snow with benzene concentration 0.4 mg/l during the 100-years period. The concentration of benzene transporting on a level of groundwater will be close to zero. The benzene concentration in soils will exceed 300 mg/kg due to washing benzene out from soils as a result of contaminant sources liquidation and clear precipitation infiltration at the end of 200 years. The benzene concentration in moisturize transporting on a level of groundwater will exceed 90 mg/l (Figure 7).

■ - 50 years, ●-100 years, ▲- 200 years
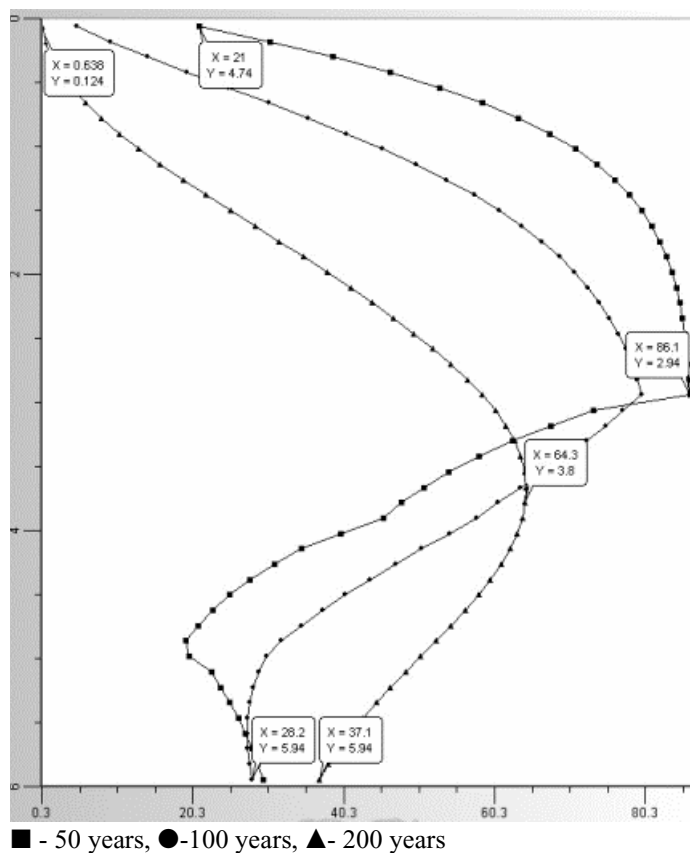
Figure 7. Benzene concentration (mg/l) in soil moisturize on the

Liquidation of contaminant primary sources will prevent the further environment pollution, however contaminants can be input from contaminated vadoze zone soils to ground water for a long time. Discharging of contaminated waters in park ponds can result in deterioration of their quality. It is shown on this example of researches, that influence of contaminant primary sources can result in significant contamination not only ground waters, but vadose zone soils too. In unsaturated zone the contaminant secondary source can be formed. The input of contaminants can proceed for a long time even at primary sources liquidation. Infiltration of waters polluted with oil products can result in contamination vadose zone soils by various components of oil, including PAH.

At an assessment of vadose zone soil hazard as contaminant secondary source of water systems, taking into account significant distinctions of physical and chemical properties of hydrocarbonic components of oil products, it is necessary to determine not only total concentration of oil product, but also individual components. It will allow proving remediation solutions, including the calculation of contaminated soils excavation volumes.

CONCLUSION

On two examples various cases of vadoze zone pollution formation and various approaches to the decision of the secondary pollution sources liquidation problem are considered. In the first case on the site of unauthorized dump

vadoze zone contamination by heavy metals was occurred as a result of warehousing the polluted waste of various genesis. The standard approach has not allowed providing an optimal variant of removing the polluted soils. The existing practice of decision-making about the ways of territory remediation does not have the preliminary analysis of polluting substance concentration change in the vadoze zone at various variants of polluted soil excavation. Numerical modeling of unsaturated flow and mass transport in the vadoze zone may be one of possible ways of such analysis, despite the simplified representation of flow and transport processes. The modeling results allowed to find out, that decontaminating of the polluted soils up to migration water parameter values happens most quickly due to excavation the sewage sludge layer and thus proved the optimum variant of contaminated soils excavation.

In the second case soil pollution of the vadoze zone by oil products and RAH in the park territory was generated as a result of primary pollution sources effect. Standard method of hazard estimation of contaminated by oil products and RAH vadoze zone soils have not been produced. The approach to an estimation of the vadose zone role as a secondary source of groundwater pollution is offered at liquidation of primary sources. The modeling of oil products in vadoze zone have shown, that even on the end of the 200-year period the concentration of the main oil products components - benzene and toluene in soil will exceed 300 mg/kg, and their concentration in the moisture inflowing to the groundwater waters level will exceed 37 mg/l and will grow further up to 90 mg/l, that is considerably above maximum allowed concentration.

The offered approach based on modeling of unsaturated flow and mass transport in vadoze zone is the first stage at an estimation of vadoze zone soil hazard as a secondary source of groundwater pollution. For acceptance of the final decision it is necessary to complete the modeling in vadoze zone by modeling of groundwater contamination prediction.

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