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## Extended Abstracts

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title: **Environmental and hydrogeological monitoring of sites contaminated with light petroleum products**

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## CONCEPTION AND GOALS OF MONITORING

Monitoring of sites contaminated with light petroleum products (LPP) represents the system of observations on qualitative and quantitative changes of LPP plumes in the subsurface in order to reveal and estimate LPP state, volume and transformation, predict LPP spreading and prevent LPP impact on soil, surface water and groundwater for estimation of environmental state and development of preventing or remedial actions.

The goals of monitoring are elaborated at the stage of research. Monitoring design must answer the following questions: 1) which characteristics and parameters are monitored; 2) which number of sampling points and their allocation is necessary; 3) which models are used to predict LPP migration.

Since LPP are immiscible fluids and can migrate in the subsurface as a liquid, a gas, an emulsion, being dissolved in water and retained in soil, monitoring of LPP contamination is rather specific and different from monitoring of groundwater contamination with dissolved chemical substances. Observation wells do not represent levels and thickness of LPP lenses on a groundwater table as well as a volume of LPP retained in unsaturated soils.

Up to date most of research into monitoring of groundwater contamination concern dissolved contaminants. In Ukraine problems of monitoring of the subsurface contaminated with LPP were examined for individual territories not taking into consideration general characteristics of petroleum product migration in the subsurface, estimation of their volume, state and transformation, and potential remediation.

Monitoring conception at different stages of research including *estimating*, *special* and *controlling* monitoring is developed.

## ESTIMATING MONITORING

Estimating monitoring is carried out during research into determination of subsurface contamination rate and environmental threat. Works are carried out into four stages:

- Distribution of contaminants in space and lithological and hydraulic properties of the subsurface are estimated by rapid field methods.
- Monitoring of the subsurface is carried out to estimate dynamics of contamination and detect LPP destruction and its rate.
- Dynamics of contamination is estimated, and contamination spreading is predicted taking into account natural biological degradation.
- Risk for objects exposed to contamination is determined.

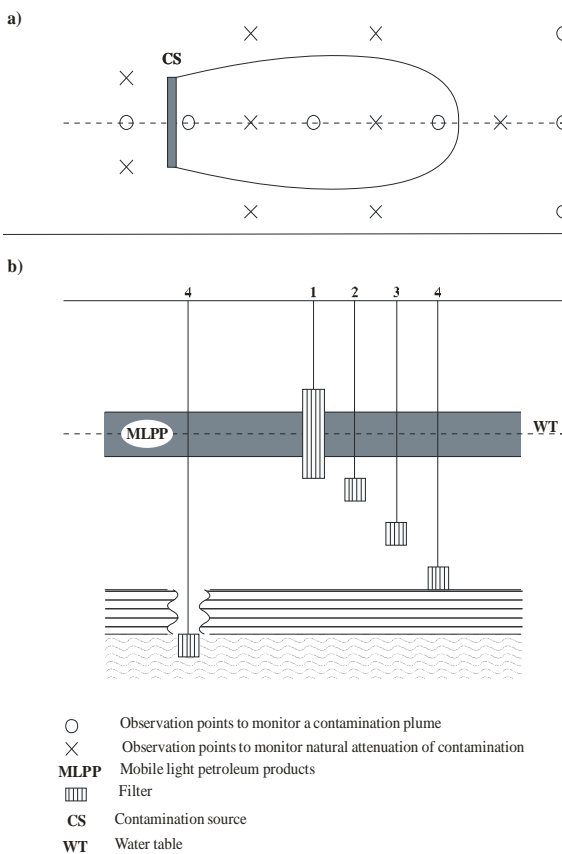
Main goals of the first stage are to establish a contamination source and objects exposed to contamination, delineate a contamination plume in subsurface air, soil and groundwater, and determine a volume of LPP in the subsurface. This stage is finished by a conceptual scheme of subsurface contamination.

The main task of the second stage is to establish stability, increase or reduction of LPP mass in the subsurface. If LPP mass decreases, it is necessary to determine the cause of this (volatilization, sorption, dispersion, or biodegradation). Geochemistry data are collected to corroborate biodegradation. In case of biodegradation concentrations of electron acceptors (oxygen, ni-

trates, sulfates,  $\text{Fe}^{+3}$ , etc.) decrease within a contaminated plume while concentrations of metabolic co-products ( $\text{Fe}^{+2}$ ,  $\text{Mn}^{+2}$ , methane, etc.) increase. High correlation between electron acceptors, electron donors, and co-products indicates that LPP mass decreases due to biodegradation.

All components of contaminated subsurface (soil, subsurface air, and groundwater) are monitored. Stable contamination plumes and plumes with a limited migration potential are monitored during one year. Maximum term of monitoring is three years to determine stability or decrease of a contamination plume. Quarterly measurements enable to represent the influence of seasonal groundwater fluctuations, precipitation, etc.

Subsurface air is monitored periodically by means of gas survey. The unsaturated zone with residual LPP is monitored periodically by sampling. Observation wells are installed within a lens of LPP and a zone of dissolved LPP (Figure 1).



**Figure 1.** The location of observation points: a) within a real or potential contamination zone, b) in an observation point.

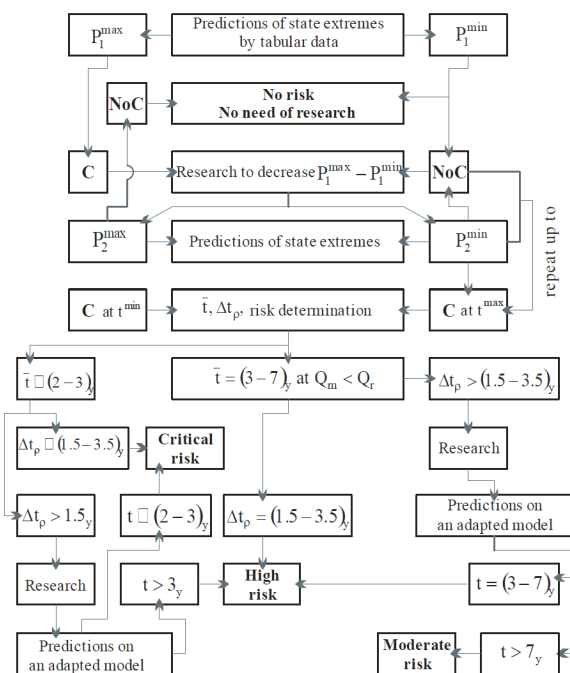
The rate of LPP biodegradation is estimated by decrease of LPP mass or concentrations using either calculation dependences in simple conditions or mass transport models in complex conditions.

Risk is determined for objects exposed to contamination, which is attended by a threat to human health, fauna and flora due to accumulation of contaminants in soil, air, surface water and

groundwater. Such objects are water-supply wells, surface water reservoirs, agricultural lands, air in places of human activity where contaminant concentrations exceed extremely limited concentrations.

The method of risk determination is based on predictions of extreme conditions by groups of parameters within possible errors accelerating and decelerating the process of contamination. Boundary values of contamination time  $t_{min}$  and  $t_{max}$  are calculated. It can be accepted as a range of possible values  $R = t_{max} - t_{min}$  with an arithmetical mean  $\bar{t} = (t_{max} + t_{min})/2$  and a mean-square deviation  $\sigma = R/\alpha_n$  where  $\alpha_n$  is a tabulated value depending on a number of estimations, and a probable error value  $\Delta t_p = 0.6745\sigma$ .

An arithmetical mean value of contamination time  $\bar{t}$  with an error  $\Delta t_p$  is used to determine risk. If  $\Delta t_p \leq T/2$ , where  $T$  is time defining a degree of risk, parameter values are reliable. Otherwise parameter values are unreliable and it is necessary to carry out added research to reduce a range of parameter errors.



- $P_1^{max}$  are initial parameters accelerating LPP spreading.
- $P_1^{min}$  are initial parameters decelerating LPP spreading.
- $P_2^{max}, P_2^{min}$  are corrected parameters.
- $C$  is contamination, **NoC** is no contamination.
- $t$  is contamination time,  $y$  - years
- $t^{max}, t^{min}$  are maximum and minimum contamination time.
- $\bar{t}$  is arithmetical mean contamination time.
- $\Delta t_p$  is a possible error of contamination time.
- $Q_m, Q_r$  are costs of monitoring and remediation.

Figure 2. The scheme of risk determination.

Crisis situation and critical, high, moderate, and low risks are defined. In a crisis situation LPP concentrations are already exceed extremely limited concentrations (ELC) during estimating works. If LPP concentrations are less than ELC at an extreme parameter error it is no risk for an object. Figure 2 demonstrates the scheme of risk determination.

### **SPECIAL MONITORING**

Special monitoring is carried out at the stage of prospecting and remediation when there is a critical or high risk of contamination for an object. A part of the subsurface where contamination spreads is studied.

The tasks of prospecting are to specify parameters of the subsurface, a volume of contamination, and the effect of natural biological degradation, choose and test remediation methods.

Parameters describing the possibility of LPP extraction, the effect of bioventilation and microbiological activity are determined by means of test pumping in all observation wells, estimation of gas permeability in soil and testing of oxygen consumption by microorganisms. Water table fluctuations are studied including a long-term rise or decrease, seasonally compensated or relatively stable water table. A soil organic analysis determines the presence and composition of LPP and physical soil properties (grain size, bulk density, porosity, and moisture) enable to identify subsurface air movement through soil.

Concentrations of BTEX (benzene, toluene, ethylbenzene, and xylene) and total hydrocarbon concentrations are determined in groundwater and subsurface air. LPP boiling points are analyzed, which enables to establish the role of volatilization.

During remediation monitoring is carried out to determine the efficiency of remediation and correct a volume and rate of works. Measurements and sampling are carried out every month or quarterly depending on velocity of remediation.

### **CONTROLLING MONITORING**

Controlling monitoring of contamination plume spreading is carried out in the subsurface when there is a moderate or low risk of contamination for an object in order to prevent a high risk.

Location of controlling observation points (COP) depends on dynamics of a contamination plume. If a contamination plume increases and an object is contaminated in 7–10 years (moderate risk), COP are located perpendicularly to a central line of the plume at the distance of contamination movement in 2–3 years (Figure 1a). As soon as a contamination plume approaches, COP are relocated at the same or corrected distance.

Controlling monitoring is also carried out within a compliance zone of objects that are potential sources of contamination in order to reveal contamination as soon as possible (Ognianik et al., 2006). LPP concentrations must not exceed ELC at the boundary of a compliance zone, which is controlled by the state regulators. Otherwise, the enterprise must pay a fine.

The problem lies in the fact that observation points are projected when there the aquifer is not contaminated yet. Qualitative and imitation approaches are developed to solve this problem (Loaiciga et al., 1992; Meyer, Brill, 1988 but they are not efficient.

We propose to locate observation points in the most sensitive nodes of mass transport models, taking into consideration boundary conditions, dispersion, sorption, biodegradation, etc. At this, relative contaminant concentration  $C_c=1$  is specified at contamination source and  $C_c=0$  at the boundary of a compliance zone. Obtained concentrations in parts of unity indicate node sensitivity to contamination. Node sensitivity is

$$W_j = \sum_{j=1}^n C_j$$

where  $C_j$  is relative contaminant concentration at  $j$ -realization of its outflow. Observation points are located in the most sensitive nodes. The problem is defined as

$$\max Z = \sum_{j \in J} W_j x_j \quad \text{given} \quad \sum_{j \in J} x_j \geq P$$

where  $j$  is an areal index of observation point location;  $J$  is a range of potential observation point location;  $x_j = (0,1)$ : 1 — if an observation point is in a sensitive node, 0 — otherwise;  $P$  is a number of observation points defined as  $\sum_{j \in J} q_j x_j \leq R$ , where  $q_j$  is the cost of installation of  $j$  observation point;  $R < S + (Q_c - Q_o)$  are reasonable money resources,  $S$  is the sum of a possible fine;  $Q_c$  is the cost of remediation within a compliance zone;  $Q_o$  is the cost of remediation within an optimal zone.

This approach was tested on the case study of the location of observation points near a sewage pond.

## CONCLUSION

- Monitoring of sites contaminated with LPP, which are immiscible fluids, is rather specific.
- The system of monitoring includes estimating, special and controlling monitoring.
- During estimating monitoring LPP distribution in components of the subsurface, transitions, rate of biodegradation are determined. The final result of estimating monitoring is risk determination for objects exposed to contamination. The method of risk determination is proposed.
- Special monitoring is carried out at the stages of prospecting and remediation when there is a critical or high risk of contamination for an object. The main tasks are to specify LPP volume, choose and test a remediation method. Monitoring data are used to identify mathematical models imitating remediation to optimize it.
- Controlling monitoring of contamination plume spreading is carried out in case of a moderate or low risk of contamination for an object and also within a compliance zone of objects that are potential sources of contamination. The location of observation points in the most sensitive nodes of the mass transport model is shown provided that costs for monitoring network location and remediation in an optimal zone must be much less than a fine and costs for remediation in a compliance zone.

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