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Using the Methods of Statistical Analysis to Determine the Safe Content of Oil Products in Gray Forest Soil

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Abstract—This paper presents an algorithm for determining the content of oil products in remediated soil that is safe for plants and microorganisms. The algorithm includes laboratory modeling of the remediation of soil samples that contain different amounts of soil products, determination of the biological parameters that provide the integral characterization of the soil state in these samples, and analysis of the results on the basis of odds-ratio statistics, which allows one to determine the content of oil products, starting from which the state of an oil-contaminated soil has no significant difference from a control soil.

Keywords: oil contamination of soil, remediation, phytotoxicity, mathematical modeling
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Oil hydrocarbons are widely distributed industrial pollutants that enter the environment as a consequence of oil leakage during oil production, transportation, and storage. Techniques that use biological methods are being actively developed in the technology for purifying soil from oil contamination. However, the residual content of oil products, whose achievement would permit the remediation process to be finished, has not yet been determined. In these circumstances, in order to estimate the efficiency of reclamation and make a conclusion about the toxicity of oil products, most studies are based on the chemical analysis of the content of oil products in soil, for example, by the methods of gas chromatography and mass spectrometry [1]. However, the decrease in the concentration of pollutants in a soil does not always mean a decrease in the toxicity of the contaminated soil [2]. Moreover, incomplete oil degradation and formation of intermediate transformation products formed at different stages of soil remediation can lead to an increase in the toxicity of a soil [3, 4]. Therefore, combination of chemical analytical and biological studies is recommended to estimate the efficiency of remediation. It is the assembly of the responses of a soil community to the anthropogenic factor that can provide an adequate picture of the soil state [5, 6].

A number of authors have recommended mathematical modeling of the functioning of biological soil objects in order to build statistically valid recommendations. Earlier, parametric models based on differential equations [7–10] were used to describe the processes of soil self purification, change in individual parameters, as well as integral assessment of the ecological soil state in the case of oil contamination [7–10]. To analyze and interpret the data that were obtained within the framework of ecotoxicological studies, non-parametric statistical methods of analysis are also applied [11–13].

The goal of this work is to reveal the content of oil products in reclaimed gray forest soil using the methods of statistical analysis.

MATERIALS AND METHODS

A gray forest soil was selected in the background territory of the Laishev region of the Tatarstan Republic for investigation. In order to create model samples of oil-contaminated gray forest soil, the soil was contaminated with separator oil at doses of 1, 2, 3, 10, and 15% of the soil weight. The separator oil was taken at the Bastryk preliminary discharge unit of the oil-and-gas production department of the OJSC Tatneft. Uncontaminated soil served as a control. The laboratory modeling of the remediation process was carried out for each of the variants of soil contamination. The introductions of the following substances were used as remediation methods: a) nitrogen fertilizer (urea) with sawdust; b) organic humus fertilizer (mature annual dung); c) Devoroil industrial biopreparation; d) tillage of soil. The doses of mineral and organic nitrogen fertilizers that were introduced into oil-contaminated soil samples were calculated according to VRD 39-1.13-056-2002 [14]. The amount of the introduced Devoroil biopreparation was determined according to the application guide. Soil samples were selected during the laboratory modeling of remediation for 7 months from the date of the contamination. The variants were modeled three times each.

The content of oil products in the soil was determined by the IR-spectrometry method [15]. The phytotoxicity of the soil was determined according to the length of the second leaf, height of the above-ground part of plants, and dry matter phytomass according to the GOST [16]. The respiratory activity and total microbial biomass [17], as well as the dehydrogenase and urease activities [18] were determined in order to characterize a soil microbial community. The parameters were all measured not less than three times.

The randomization method was used in order to build the extended sample of the results of the experiment. Non-linear generalized additive models (GAMs), which were implemented in the mgcv package, were used to describe the non-linearity of measuring the indicators in time [19]. An algorithm for revealing the value of the content of oil products that does not exert a negative effect was implemented as a program in the environment of the R statistical system [20].

RESULTS AND DISCUSSION

The stabilization of a microbial community and level of phytotoxicity that did not differ significantly from that of uncontaminated soil were used when determining the safe residual content of a remediated soil. A large number of samples that differed in their contents of oil products and biological activity, as well as their content of oil products, were obtained in order to determine the safe content of oil products. When the modeling was performed, soils with a different initial content of oil products were used and different methods for their remediation were applied. The laboratory modeling of the remediation processes was performed for 7 months, during which samples were selected in which the content of oil products, respiratory, dehydrogenase, and urease activity, total microbial biomass, dry matter phytomass, length of the second leaf and above-ground part of the test plants were determined. The indicated parameters were chosen as those that are most often recommended during the analysis of oil-product contaminated soils and reflect the state of soil adequately [3, 6, 21–24]. The results are presented in the research of Akhmetzyanova et al. [25]. In sum, 1080 samples were selected and analyzed. In order to determine the safe content of oil products that can be used during remediation under field conditions, it was necessary to ascertain the dependence that binds the content of oil products and the parameter that reflects the ratio between the values of biological parameters in the contaminated (experiment) and background (control) samples. Proceeding from the fact that natural factors simultaneously affect the organisms of the contaminated and background areas under the field conditions, this approach, which is based on the application of relative values, permits the values of the safe content of oil products in soil to be considered as acceptable for the field conditions.

To determine the safe content based on the obtained empirical data, the model for the temporal change in the content of oil products, state variables of a soil microbial community, and level of phytotoxicity were built at the following stage. The behavioral models of analyzed parameters for the variant with 3% contamination and application of Devoroil were presented as an example in Fig. 1.

The data that were obtained for each parameter of the model at each specific instant were used to check the statistical hypothesis that states that the values that were obtained in the experiment do not differ from the control more often that the values of the control between each other, which indicates that there is no effect from oil products.

Odds-ratio statistics were used for this purpose (*OR*). The *OR* was calculated using the following formula:

$$OR = (n_{11}/n_{12})/(n_{21}/n_{22}),$$

where n_{11} and n_{12} are the number of the results of measurements in the experiment that differ from the control significantly and insignificantly and n_{21} and n_{22} are the number of the results in the control that differ from each other significantly and insignificantly.

At the following stage, the values of the *OR* statistics, namely, those of the left boundary of the *OR* confidence interval that were obtained when checking the accepted hypothesis, were correlated with the actual content of oil products in the experimental variant at each instant.

Subsequently, supposing that distinctions for all the observed parameters are simultaneously absent if there is no effect of oil products, the obtained values of *OR* are combined and thought to be a sample from a single assembly, for which the model of the position of the *OR* statistics with respect to the critical value of the indicated hypothesis, which depends on the concentration of oil products, is built. Thus, if the confidence interval of *OR* include one (a 1 : 1 odds ratio), then the values that were obtained in the experiment do not differ from the control more often than some values of the control from others, i.e., the results of the experiment must not be considered to be significantly different from the results of the control.

To obtain the position of the left boundary of the confidence interval for an arbitrary concentration of oil products, the results (for all indicators and all concentrations within the framework of each remediation method) were all combined and the model of the position of the left boundary with the corresponding confidence intervals that took into account different positions of this boundary for different indicators was built. The intersection of the model line with the zero value line (at the log (*OR*) scale) corresponds to the content of oil products, starting from which there are no grounds to believe that the indicators of the soil state in the experiment differ from the indicators of the control. The highest concentration (7.78 g/kg) was fixed for the tillage remediation method; if humus is introduced, a greater decrease in the content of oil products (to 3.54 g/kg) is required for a community to achieve a stable state. These distinctions can be first of all explained by the fact that the introduction of humus and other organic substrates that are sources of nutrients significantly stimulates the growth in the population and activity of microorganisms [26–31]; as

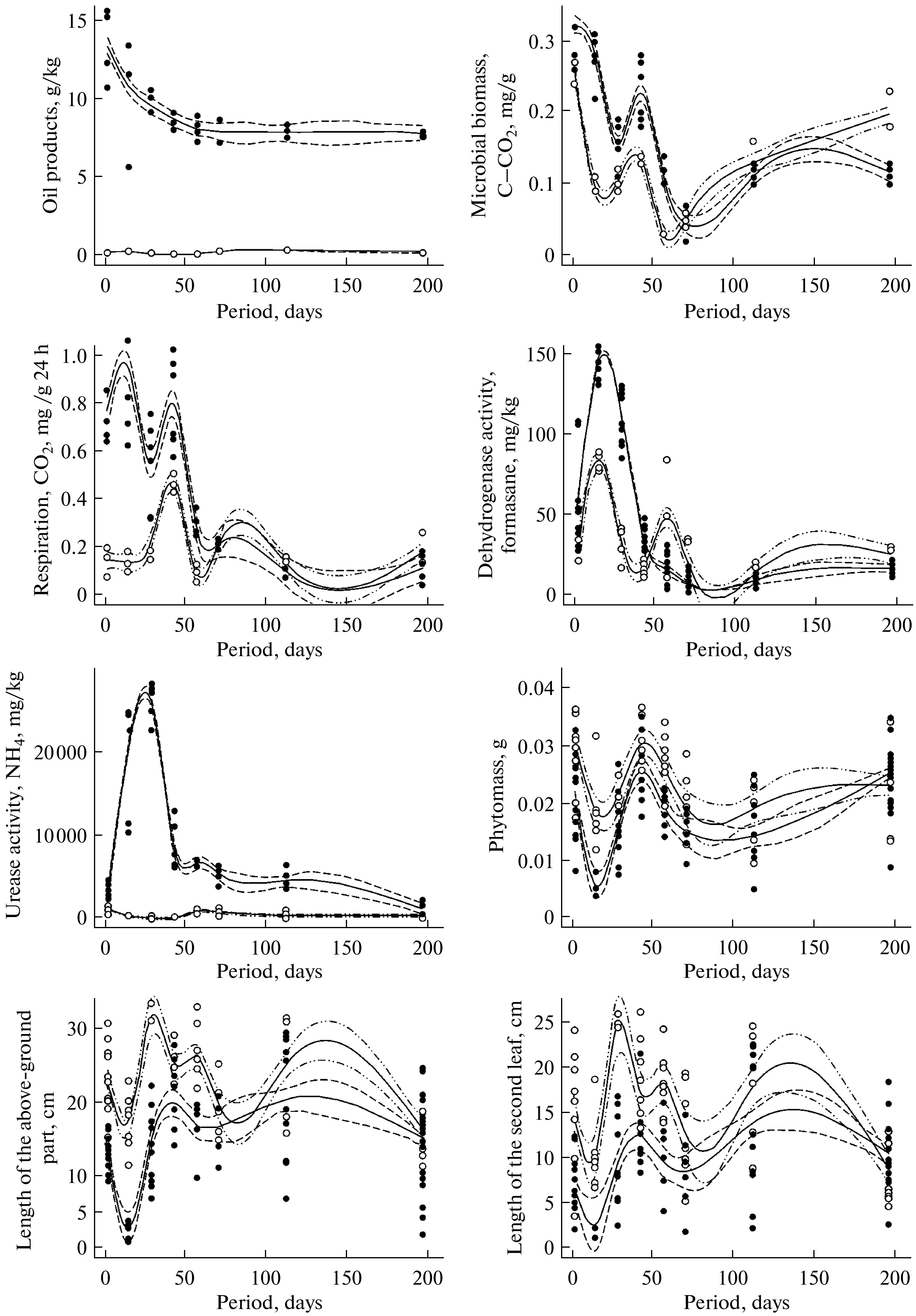

Fig. 1. Models for measuring the analyzed parameters for the variant with 3% contamination and application of Devoroil (the gray and black colors denote the control and experimental variant, respectively).

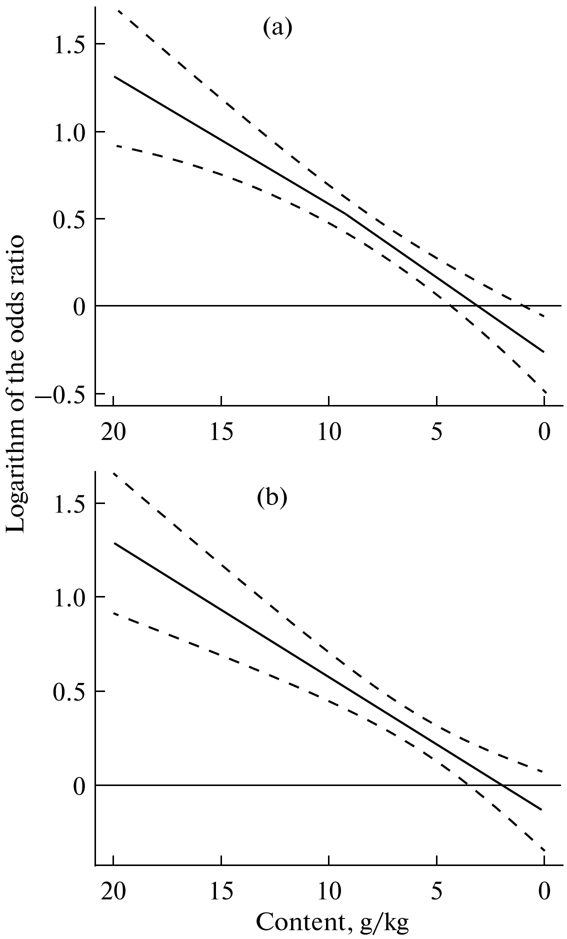

Fig. 2. Model estimates of the position of the left boundary for the 95% confidence interval of the odds ratio with respect to the content of oil products in soil: a, with the application of urea and sawdust; b, with the application of Devoroil. Logarithmic scale for *OR*.

a result, the distinctions from the parameters of the control variant are retained for a longer period. Secondly, the application of different remediation methods does not result in the formation of compounds with different toxicities, which causes the changes in the soil characteristics as a whole. Actually, many authors believe that different sources of organogenic elements exert a different influence on the efficiency of hydrocarbon degradation, which is due to their different biological accessibility and toxicity [4, 5]. In addition, soil organisms are affected by phytotoxins formed in soil in the process of its remediation [21, 32]. Figure 2 presents the model estimating of the position of the left boundary for the confidence interval of the odds ratio depending on the content of oil products for the variants of remediation with the application of urea with sawdust and Devoroil.

Taking into consideration that a complex of methods is most often used during soil remediation under actual conditions, the assembly of data of all reclamation methods was analyzed at the conclusive stage

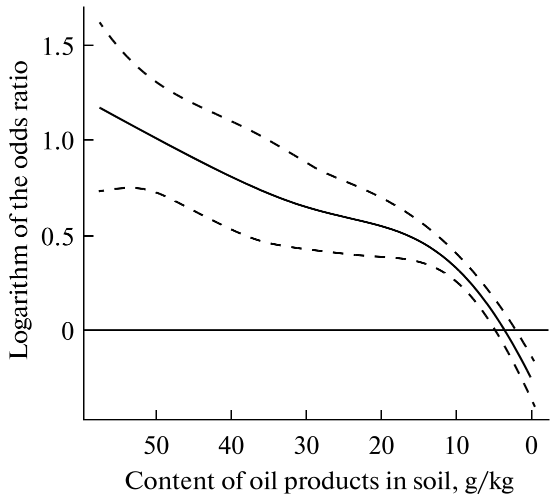

Fig. 3. The model estimate of the position of the left boundary for the 95% confidence interval of the odds ratio; this was calculated according to the complex of indicators using a logarithmic scale.

(Fig. 3). The interval of the content of oil transformation products that formed under the investigated methods for remediation of oil-contaminated gray forest soil, starting from which the content of oil products could be thought safe, was found to be 3.08–4.83 g/kg. The obtained value can be used as a basis: this value should be verified during the remediation process under field conditions in order to accept it subsequently as a standard.

CONCLUSIONS

Thus, our algorithm, which includes the laboratory modeling of samples that contain different amounts of oil products, the determination of their biological parameters that characterize the soil state integrally, and analysis of the results based on odds-ratio statistics permits one to determine the content of oil products starting from which the state of an oil-contaminated soil does not differ significantly from the control. This content can be considered as safe for a soil community and remediation can be regarded as finished.

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