CONTAMINATION OF THE GEOLOGICAL ENVIRONMENT – REMEDIATION OF UNSATURATED ZONE, COMPARISON BETWEEN MATHEMATICAL MODEL AND ACTUAL DATA

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Hazardous substances (heavy metals) contamination of agriculture soils does not represent a serious issue in the Czech Republic (S á ň k a et al., 2002). Increased occurrence of hazardous substances, especially hydrocarbons is observed in sense with the accident releases of dangerous substances. This is the reason for tracking substances mobility and remediation techniques with the focus on elimination of the transfer to plants. This contribution is focused on the proposal of optimal remediation technique during an accidental large-scale spillage at the gasoline pipeline near the village Polepy in August 2001. The massive contamination of soils and groundwater was identified; the spill was approximately 86 m^3 of unleaded gasoline. The excavation of contaminated soils and groundwater – pump and treat – was performed immediately. The soil vapor extraction wells were performed in the next step (K ř í ž, W i t t l i n g e r o v á, 2004). The mathematical model of remediation including the placement of the extraction wells and the forecast of the level of VOC gas concentration in time has been done as well (C h a l o u p k a, 2001). Remediation of the soil gas was concluded and performed. The measurements enable comparison of the model solution and the real numbers obtained from the sampling during the remediation process. Model solution is in accordance to the real conditions on-site during the remediation. The decrease of VOC concentrations has been proven both by the model solution and the remediation itself as well. Model solution enables the assessment of key remediation indicators like the forecast, time behavior of VOC concentrations and the total remediation duration. Success of the described model depends on the presumption of accuracy of the soil permeability and the preliminary soil gas sampling.

geological environment; contamination; soil vapor extraction; mathematical model

INTRODUCTION

Soil Vapor Extraction (SVE) is an effective technology used for remediation of the volatile organic compounds (VOC) from the geological environment. The extraction wells are installed in impacted areas and the contaminated air is siphoned off-site through the distribution system. VOCs are adsorbed in the filter with active carbon or are burnt by catalyst units on-site. The efficiency of remediation depends on the type of pollution and the subsurface conditions. Suitability of using SVE can be evaluated by field tests or mathematical modeling. Model simulation has advantages and also disadvantages. The basic advantages of SVE are: forecast of VOCs in time, lower costs and promptness.

MATERIAL AND METHODS

The used technology for remediation is SVE; this technique is used for vapor extraction from the contaminated soils. It is appropriate for decontamination of volatile and some semi-volatile substances from the unsaturated zone. The SVE is appropriate for removal of substances that have partial pressure of vapors in a 20 °C larger than 14 mm on Hg centigrade (around 1.8 kPa) and the Henry's constant exceeds 102 Pa m^3.mol^{-1}. The volatile substances release a significant weight ratio of the compound from the water solution into a vapor phase. Based on temperature and pressure conditions the evaporation creates one of the major mechanisms for migration of volatile organic substances (J o h n s o n et al. 1990a, b). Due to a large portion of VOCs in the designated area, the remediation technique of in-situ SVE was used.

The contamination of soil by volatile contaminants spreads through the soil types. It may be assumed that in the first phase the contaminant will spread between gas (soil gas), liquid (groundwater) and solid parts of soil environment. In case of static conditions the distribution may be described by a set of balanced parameters: water solubility, vapor pressure, Henry's constant and sorption to soil particles. The above mentioned is in accordance with the static environment before the remediation process. In case the static conditions change into dynamic (e.g. vapor extraction from the contaminated soil) the contaminant distribution changes in link with the extracted vapor. The result of vapor extraction from the contaminated soil is gradual decrease of the contaminant in gas, liquid and solid parts of the soil.

Basic factors designating the venting effectiveness are: physical and chemical attributes of the contaminant,

air-flow in the contaminated soil, temperature of soil gas, water saturation, pollutant concentration, whether the environment is homogenous or heterogeneous, presence of fractures and permeable zones, the soil sorption capacity, groundwater level, appropriate placement of extraction wells.

Application of in-situ SVE method must be preceded by designating the main project parameters (S h e p - p a r d et al., 1992), which are: number, location and size of extraction wells, remediation time estimation. The most significant parameter recognized prior to venting was the permeability of the soil type. The parameter indicating the soil permeability is the permeability coefficient K (m^2). In case of getting a constant speed of vapor extraction Q – the actual pressure P changes in time as follows:

$$P = \frac{Q \cdot \mu}{4 \cdot \pi \cdot m \cdot K} \cdot \left[-0.5772 - \ln\left(\frac{r^2 \cdot n_a \cdot \mu}{4 \cdot K \cdot P_{atm}} \right) + \ln(t) \right]$$

where:
m (cm) – extraction well diameter
μ (g.cm^{-1}.s^{-1}) – soil gas dynamic viscosity
r (cm) – distance between the control and extraction wells
P_{atm} (g.cm^{-1}.s^{-2}) – atmospheric gas-pressure
n_a (%) – gas saturation
Q (cm^3.s^{-1}) – air flow

Unit of permeability K is Darcy (1 Darcy = 10^{-8} cm^2), gradient S (g.cm^{-1}.s^{-2}) is proportional to the permeability coefficient:

$$K = \frac{Q \cdot \mu}{4 \cdot S \cdot \pi \cdot m}$$

The individual coefficients of permeability K for individual control wells are then averaged and this averaged value shows the parameter for the individual drill surrounding. Further if we assume a linear relation between the actual pressure P and values log (r) then we can create a regression through n monitoring drills:

$$p = a \cdot \log(r) + b$$

By approximating to zero pressure value we can than find out the distances R during which the vapor extraction will not take effect. This distance matches the drill reach and it can be found out as follows:

$$R = 10^{-\frac{b}{a}} \text{ (when Q = const.)}$$

Assuming that the relation is linear between drill reach R and flow speed Q than for any chosen flow speed the reach of any chosen drill can be found out as follows:

$$\frac{R_1}{Q_1} = \frac{R_2}{Q_2} = \ldots = \frac{R_n}{Q_n}$$

Minimum amount of extraction wells (N_{min}) needed for remediation of contaminated area of A (m^2) can be found out as follows:

$$N_{min} = \frac{A}{\pi \cdot R^2}$$

There are several basic conditions for correct usage of SVE – number and location of extraction wells and the remediation timeframe. It is possible to establish the remediation time frame for designated target values. Based on remediation time frame, it is possible to estimate some parameters of treatment unit. Several commercial numerical mathematical model solutions are available. These solutions may be used with requested accuracy for simulation of contaminant transport in the framework of SVE. In our case the Waterloo's hydrogeological software AIRFLOW / SVE was used. This software enables monitoring of all requested parameters.

The model is based on assumption that the contaminated soil is homogenous in its full volume. The transport processes in progress during soil airflow are very slow; in this case the soil conditions are close to equilibrium. During the remediation the soil characteristics do not change significantly. In connection with the on-going processes no other remediation is in place (e.g. bioremediation).

The used model solution was implemented after an accident and took in mind the preliminary knowledge of the contamination on-site. The site was divided into fields A, B and C where the active SVE technique was applied. For comparison of the model and real data fields A and C were used. These fields had more quality data sampling files regarding VOC's concentrations on input to the vapor treatment unit.

Unsaturated zone is formed by primary loess (0–6 m blg.); Quaternary fluvial sand-gravels (6–7 blg.); Cretaceous limy sandstone (7–10 m blg.) and claystone (10–12 m blg.). Groundwater level is approximately 10 m below the ground.

The contaminant is the automotive unleaded gasoline, which impacted the geological environment after the incident of the pipeline (K o c h, 2001).

The SVE system is constructed by the vertical extraction wells in the fields A, B and C. Vertical extraction wells were drilled to 10 m blg. and terminated in the claystones. The wells are connected to the system and exhausted to the catalytic treatment unit (fields A and C). Total air flow in each system is approximately 1000 m^3 of air per hour. Negative pressure at the treatment unit input is 0.75 kPa.

RESULTS AND DISCUSSION

Model solution

The AIRFLOW /SVE hydrogeologic software (G u i g h e r et al., 1995) was used for the flow simulation and contaminant transport in the unsaturated zone. The calculation provides the pressure conditions in the geological environment and remediation trend – forecast in time.

The well pressure was 0.75 kPa, well screen 2–10 m groundwater level at 10 m below the ground. Lithological description was obtained from the drilled wells.

Description of unsaturated zone and contaminant was used from the empirical datasheet (Users Guide – The Hydrocarbon Spill Screening Model, 1992) Evaluation of the gas VOC concentration decrease in the soil – field A (1500 days of continuous operation of the SVE system) (Fig. 1). The curve shows the VOC concentrations in the model well during the standard conditions (average preliminary concentration 6.150 mg of VOC/m^3). The maximum decrease of the VOC concentration will be achieved after 700–800 days of system operation.

After that the preliminary VOC concentration decreased approximately by 80% and the SVE system became non-effective.

Evaluation of the gas VOC concentration decrease in the soil – field C (1100 days of continuous operation of the SVE system) (Fig. 2). The curve shows the VOC concentrations in the model well during the standard conditions (average preliminary concentration 3500 mg of VOC/m^3). The maximum decrease of the VOC concentration will be achieved after 800–900 days of system operation.

This system allows the effective/meaningful limit value for using SVE for soil remediation to approximately 200–400 mg VOC/m^3. It will be essential to use other techniques for further decreasing of the VOC concentration in the soils.
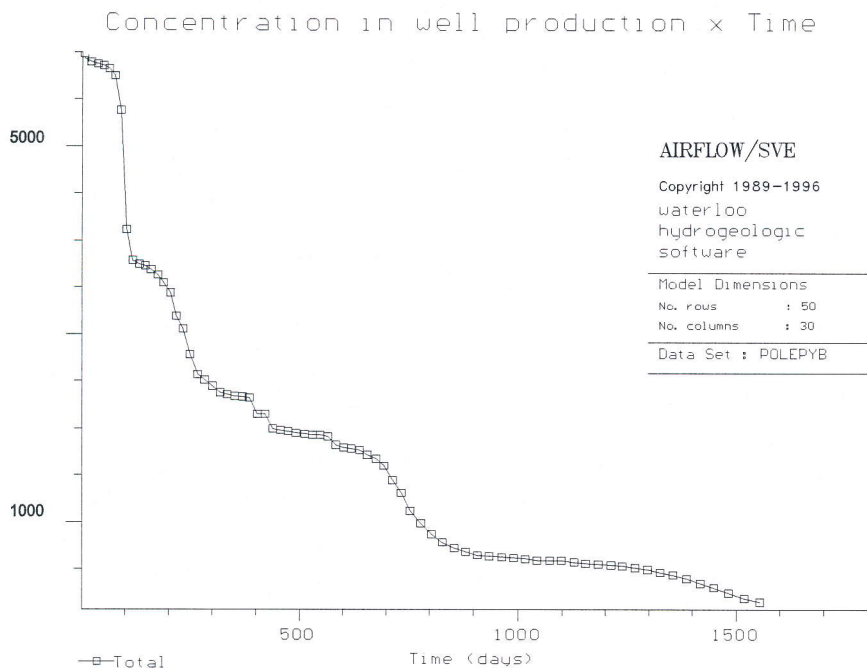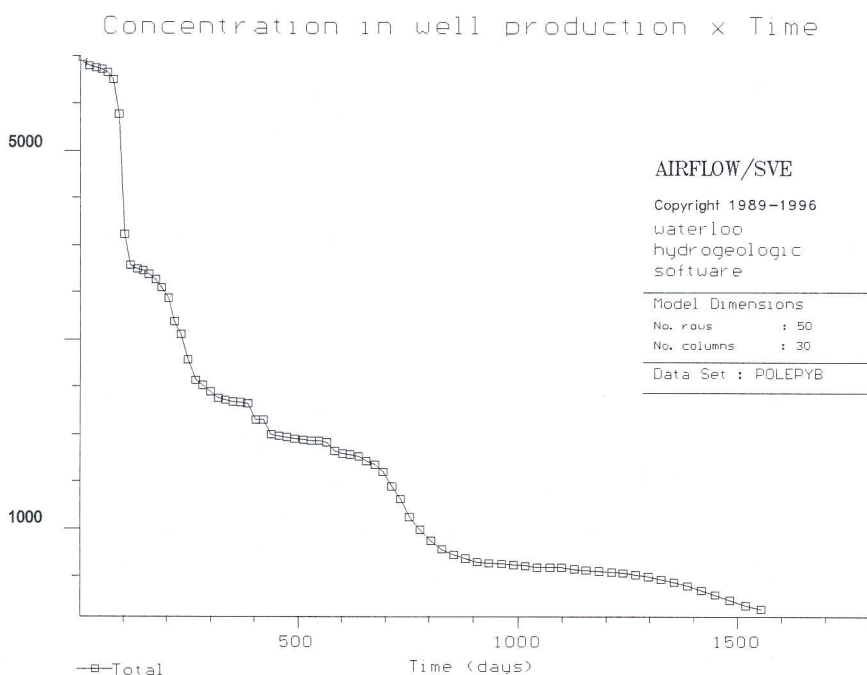

Fig. 1. Remediation forecast – field A (mg VOC/m^3)

Fig. 2. Remediation forecast – field C (mg VOC/m^3)

Real remediation data

Post accident remediation started in January 2002. The target value for A field was set to 800 mg of VOC/m^3. In June 2003 the operation of the mobile catalytic unit KOS 1000/500 was terminated. Two horizontal drains used for infiltration of biological preparation were installed in the field A. Soil gas samples taken in October 2004 did not exceed 5.5 mg VOC per m^3 of air.

The target value in the C field was set to 200 mg of VOC/m^3 (Fig. 3). The trend of concentrations in this field was significantly decreasing. The maximum concentration of VOC in October 2004 was 41.1 mg VOC per m^3.

The model VOC concentration values were subtracted and inserted to common graph with the real numbers in the A and C fields (Figs 4 and 5). Compared duration was the period between January 2002 and July 2003 – 17 months.

Preliminary concentrations in model solution represent the average VOC concentrations in all extraction wells in designated fields during the installation period. The real preliminary concentration is the VOC concentration value in the entrance to the catalytic unit. These values are comparable.

Doubled preliminary VOC concentrations can be observed in field A in the model solution which is probably caused by "fresh" VOC in the soil immediately after the accident. The trend of VOC decrease is almost identical; the difference is in model and real numbers.

The field C has almost triple preliminary VOC concentration in the real remediation, which is probably caused by "fresh" VOC in the soil immediately after the accident.

Both curves are equalized approximately after two months of remediation, and then the trend is almost identical and satisfactory. The explanation of the transition of VOC concentrations in such a short time period cannot be clearly identified. During the soil gas extraction the most volatile hydrocarbons are released first – in case of the automotive gasoline, which represents a typical mixture of hydrocarbons, it is an assumable explanation. The most volatile VOC are also more "willing" to adsorb to active surface in sampling tubes and such differences could be observed.

Result correlation was performed using the Microsoft Excel software – statistical function Correl and the degree of correlation is expressed by the correlation coefficient. For analysis in the first case the numbers from model field A were used and in the second case the C field numbers were used. If we mark (name) the Zone A (C) as x_i and Model A (C) as y_i and we determine the mean value marked as $\bar{x}$ and $\bar{y}$ for the variables x and y, and standard deviation s_x and s_y than:

variable s_{xy} defined as $s_{xy} = \dfrac{1}{n}\sum_{n=1}^{n}(x_i - \bar{x})(y_i - \bar{y})$ is called **covariance**

and variable r_{xy} defined as $r_{xy} = \dfrac{s_{xy}}{s_x s_y}$ is called **coefficient of correlation**.

Coefficient of correlation presents degree of correlation between x a y.

If $r_{xy} = 0$, there is no relationship between the variables.

If $|r_{xy}| = 1$, there is the functional relationship between the variables.

It is commonly assumed that if

$r_{xy} < 0.3$ the degree of correlation is small and it cannot be taken into account;

$0.3 \leq r_{xy} < 0.5$ indicates mild degree of correlation, in case the assumed error is small;

$0.5 \leq r_{xy} < 0.7$ indicates significant degree of correlation;
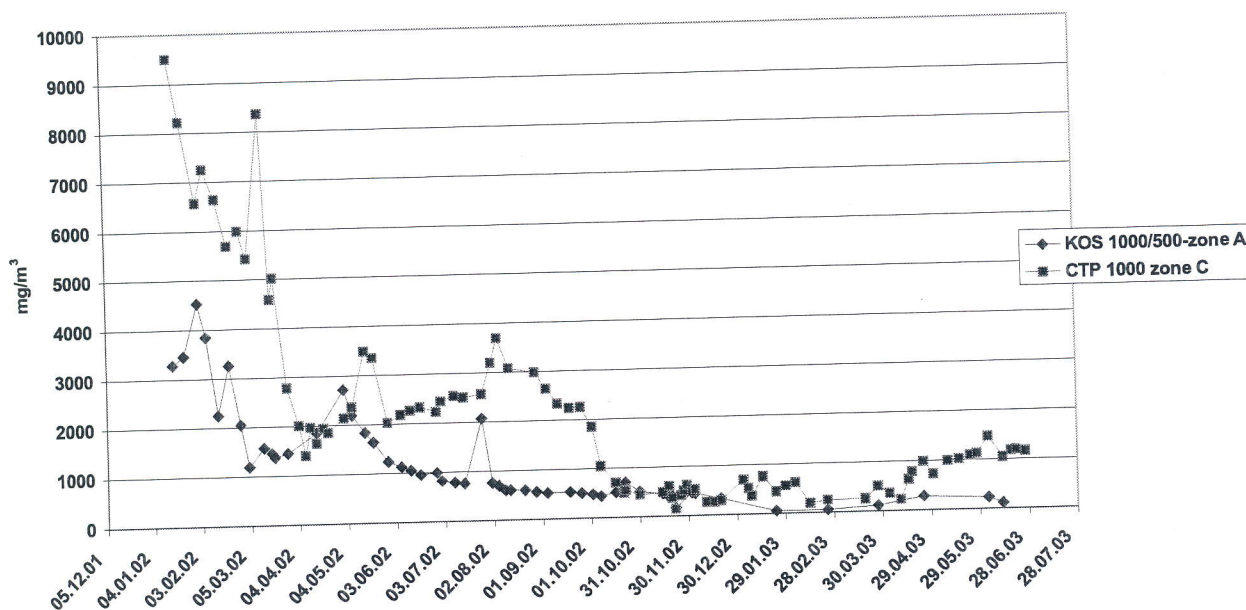

Fig. 3. Real behavior of maximum VOC concentrations between January 2002 and July 2003 (Dekonta a.s.)
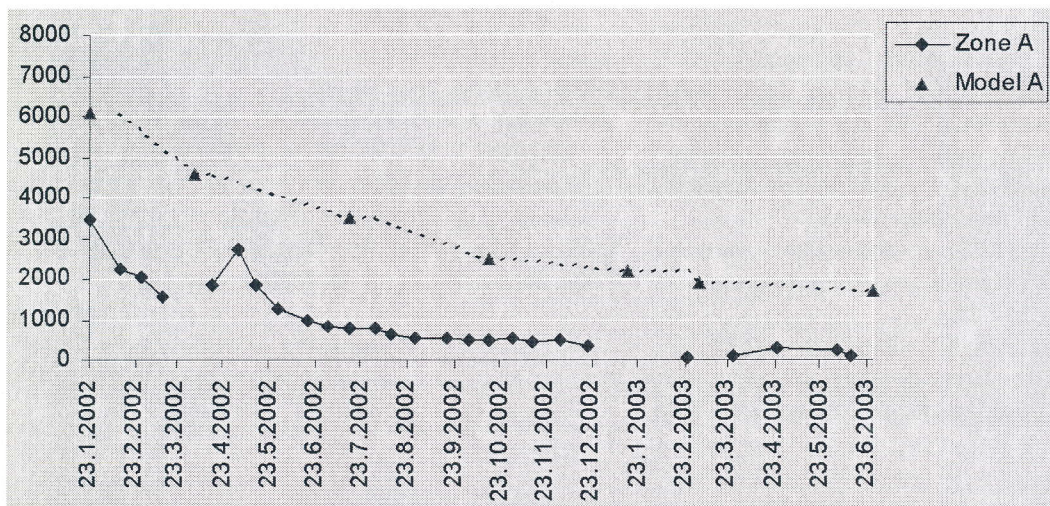
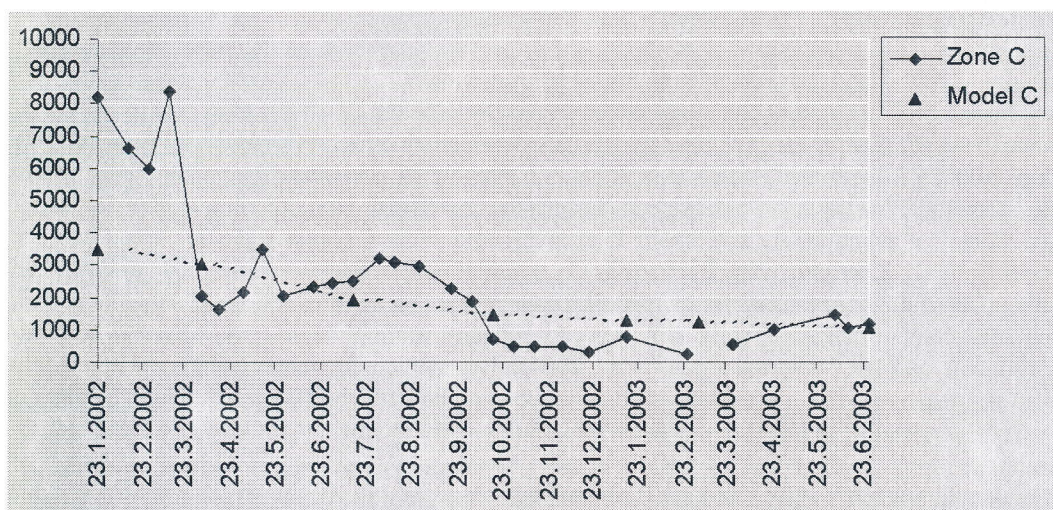Fig. 4. Field A – real and model values of VOC concentrations

Fig. 5. Field C – real and model values of VOC concentrations

$0.7 \leq r_{xy} < 0.9$ indicates high degree of correlation;

$0.9 \leq r_{xy}$ indicates very high degree of correlation, very high level of relation between the variables.

Degree of correlation calculated in the field A is 0.9789635 (very high degree), on the field C is 0.8210199 (high degree).

CONCLUSION

Performed model solution reflects the real trend of concentrations on monitored fields A and C. The trends of VOC decrease are identical and accurate. Model solution is an appropriate tool for forecasting VOC decreases in time and the remediation duration.

Key elements of the successful use of the mathematical modeling are: accurate determination of soil permeability and correct preliminary soil gas sampling.

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Kontaminace horninového prostředí – porovnání matematického modelu sanace nesaturované zóny a skutečného průběhu sanačních prací.

Kontaminace zemědělských půd těžkými kovy nepředstavuje závažný problém (S á ň k a et al., 2002). Přesto se setkáváme se zvýšenými výskyty rizikových prvků v souvislosti s havarijními úniky rizikových, zejména ropných látek. Proto se sledují mobility a možnosti sanace znečištění s cílem omezit transfer kontaminantu do rostlin. Příspěvek řeší návrh optimální sanační metody likvidace havarijního znečištění ropnými uhlovodíky na havárii produktovodu u obce Polepy v srpnu 2001, kdy došlo k masivní kontaminaci horninového prostředí ropnými uhlovodíky (benzin typu Natural). Kontaminovány byly zeminy i podzemní vody v širokém prostoru, do horninového prostředí uniklo cca 86 m^3 benzinu. V první fázi řešení následků havárie bylo provedeno odtěžení kontaminovaných zemin a zahájeno ochranné čerpání podzemní vody. Dále byly instalovány ventingové vrty pro odsávání kontaminovaného půdního vzduchu (K ř í ž, W i t t l i n g e r o v á, 2004). Byl zpracován matematický model sanace optimálního rozmístění ventingových vrtů a prognóza vývoje sanace půdního vzduchu (C h a l o u p k a, 2001).

Sanace půdního vzduchu na lokalitě je ukončena a měření umožňují provést srovnání modelového řešení s realizovaným sanačním zásahem.

Modelové řešení odpovídá reálnému stavu vývoje koncentrací na sledované lokalitě. Pokles úrovně koncentrací uhlovodíků je prokázán u modelového řešení i v praxi. Modelové řešení sanačního zásahu umožňuje posouzení hlavních faktorů sanace, jako je prognóza a průběh poklesu koncentrací a délka sanace. Úspěšnost použití matematického modelu spočívá v přesnosti stanovení propustnosti prostředí (které je jedním z hlavních vstupních údajů) a v přesném vstupním vzorkování půdního vzduchu.

horninové prostředí; kontaminace; soil vapor extraction; matematický model

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