Spatial and Temporal Evolution in the Unsaturated Zone of Pollutants Resulting from Accidental Discharges of Petroleum Products

Alexandru Florin Simion¹, Angelica Călămar¹, Sorin Simion¹, Marius Kovacs¹

¹ National Institute for Research and Development in Mine Safety and Protection to Explosion – INSEMEX Petrosani, 32-34 G-ral Vasile Milea Street, 332047, Petrosani, Hunedoara County, Romania

alexandru.simion@insemex.ro

Abstract. The exploitation and processing of oil resources are factors of regional progress and development; in this regard, the final products resulting from exploitation and subsequent refining can be accidentally split on the ground destabilizing the relationships between flora, fauna, water and soil, generating irreversible effects on terrestrial and aquatic ecosystems. The impact of the effects generated by petroleum products on soil and water resources is limiting nature and imposes severe measures to restrict the resources used for economic, administrative and consumption purposes. Experimental research involves the usage of geostatistical methods for modelling the unsaturated area and the usage of specialized applications for estimating the dispersion of pollutants in the studied area based on an accidental pollution scenario. The application of the method used in the areas with a significant risk of contamination (oil fields) it aims to identify the movement of the contaminant at various times and concentrations in order to choose the best measures to reduce and minimize pollution of the unsaturated (vadose) zone. The objectives of the reduction and minimization measures are to limit the transfer of contaminants in the saturated area or to the strategic drinking water reserves. The applied method supports researchers, hydrologists, hydrogeologists, environmental engineers who want to deepen the transition elements of the pollutant in the unsaturated area, the phenomenology and dispersion of pollutants in waters located in the unsaturated area and the problems caused by pollutants on the environment.

1. Introduction

The waters from the unsaturated (vadose) area accumulate in the first horizon of porous rocks, being fed at the regional level from the waters coming from precipitations and the neighbouring hydrogeological reservoirs [2]. The vadose zone extends from the land surface to the underground water table. It also includes capillary fringe, where pores may actually be saturated [4]. Areas of the vadose zone above the capillary fringe may temporarily be saturated due to surface ponding of water or because of the development of perched water tables above relatively low permeability soil layers [4].

Locally, groundwater is fed by the flow of surface water (rivers, lakes) through permeable formations and condensation of water vapour in rock pores. The waters that supply the ford area bring an intake of dissolved gases and minerals that is directly reflected in the quality of these waters with consequences on the use of water resources.
The conditions of transport and accumulation of pollutants are strictly determined by the stratigraphic complexity made up of the lithological variations of the lands, by their geological structure and by the thinning of the lithological layers during the geological eras. The anisotropy of the lithological layers creates a variability of the transport of pollutants in the ford area, so the contaminants discharged on the soils have a hydrodynamic behaviour closely related to the physical, chemical and biological characteristics of the mineral matrix [5].

Groundwater, unlike surface water, is much more mineralized and poorer in biological elements, are difficult to influence (pollutable) by natural and anthropogenic factors due to the low speeds of water flow through the lithological structure. Once polluted, these waters have a low resilience due to the reduced processes of dilution and natural self-purification, instead, in the lithological composition, there are processes of sorption of petroleum products on the mineral matrix and their organic transformation (degradation) by biochemical processes. The method of decontamination of these waters also involves an implicit depollution of the soils through complex processes and procedures that have a long time in terms of time and generate very high costs [7].

2. Location and description of the studied area
The studied region is located in the central area of Hunedoara county being pedologically composed of podsol soils (podsols, brown feriluvial and acid soils). The identified lithological formations are represented by a mixture of sedimentary rocks (sandstones, conglomerates, limestone, clays, sands, marls and gravels) which generate an accumulation of water from precipitation in the upper layers of the ford area intensifying the reduction of trivalent iron.

The topography of the land varies from a maximum altitude of 478 m to 451 m, measured from the level of the Black Sea with an average slope of the land of 1.35% in the direction E ÷ W. The surface of the studied land is 3457 m² (Figure 1) being located in an intramontane area opening to a depression.

The precipitation regime in the studied area varies between 600 ÷ 750 mm / year, and the average monthly temperature varies between 4 ÷ 25 °C. From the point of view of flora and fauna, the area is dominated by herbaceous vegetation with small areas of shrubs, the area being used by existing habitats as a transit area between regional ecosystems.

![Figure 1. Topografical data of the studied area](image)
The predominant economic activities are related to the raising of animals and vegetables in the field, the area being crossed by a European road that is transited by vehicles transporting petroleum products to supply the tanks, also in the region there is a fuel distribution station with two tanks—buried horizontally.

3. Materials and Methods
Land degradation is any form of deterioration of the natural potential that affects the integrity of the ecosystem, either in terms of reducing sustainable ecological productivity or in terms of the native biological reserve, maintenance and resilience. Land degradation is implicitly manifested on groundwater as well because of the physical or chemical contamination of one of them can generate irreversible effects on the other.

The spatial and temporal evolution of petroleum products in the unsaturated area resulting from accidental (oil) discharges, involves diversified research on the lithological structure and physicochemical processes that take place in the unsaturated area. From a methodological point of view, the research must include data on the lithological and stratigraphic profile, periodic observations of the hydrological and hydrogeological regime as well as the interaction between the pollutants and the mineral matrix [6, 8].

The modelling of the unsaturated (vadose) area was performed by collecting lithological data from vertical geological drilling according to the SR EN 1997-2 standard. These were performed by continuous logging in a dry or humid environment with sample recovery to determine the nature and type of lithological formation encountered [1, 3]. Data obtained from geological drilling (Table 1) were correlated with the average hydrostatic level of groundwater monitored quarterly in piezometric drilling to build the digital model of the local underground hydro structure.

| Borehole number | Northing | Easting     | Elevation | Water level | Total depth |
|-----------------|----------|-------------|-----------|-------------|-------------|
| FG 1051         | 355,456.948 | 443,286.351 | 469.24    | 12.6        | 47          |
| FG 1052         | 355,473.305 | 443,994.140 | 469.67    | 11.3        | 52          |
| FG 1053         | 354,826.252 | 443,248.229 | 470.72    | 16.4        | 51          |
| FG 1054         | 355,040.251 | 443,711.255 | 456.84    | 8.3         | 37          |
| FG 1055         | 354,906.475 | 444,076.412 | 453.59    | 15.8        | 43          |

The digital model of the hydro structure was made using the RockWorks version 15 application, using data on elevation, the thickness of each lithological layer, type of lithological formations, average hydrostatic level and maximum drilling depth (Figure 2a). From the digitally formed model were obtained with the help of the interpolation method "Kriging" with manual variogram of Gauss-Nugget type, surfaces in a 3D format that delimit the digital model of the unsaturated area (vadose) from the digital model of the hydro structure.

The hydrostratigraphic model (Figure 2b) that allows the delimitation of the unsaturated area (vadose) from the saturated area (aquifer) and the bedrock, by extrapolating the data obtained from geological drillings to generate four surfaces:

- The roof of the unsaturated area (land elevation);
- The bed of the unsaturated area (vadose) / The roof of the aquifer
- Aquifer bed / Bed rock roof;
- Bed rock
The stratigraphic model (Figure 2b) made after inserting the lithological textures in each borehole was obtained by the Kriging interpolation method. The extrapolation of the lithological compositions was performed with a probability of occurrence of each lithological type higher than 40%. The stratigraphic model obtained provides essential data on the thickness and length of each lithological texture so that volumes can be calculated for each lithological layer or the entire model.

To simulate a concentration of pollutants using the unSAT suite application, a stratigraphic section of an exciting area must be obtained, and the predominant lithological typology of the obtained profile chosen (Figure 3).

Conglomerates and sandstone represent the predominant lithological textures in the lithological section. These are consolidated sedimentary rocks that give the unsaturated (vadose) area a low permeability. The reduced slope of the topographic surface, the low permeability of the rocks that make up the unsaturated area and an average precipitation regime, reduce the rate of pollutant transfer to aquifers.

An special roulette was used to conduct field research to measure the hydrostatic level periodically, and a portable GPS was used to refer to the boundaries of the field and the geographical location of each borehole. The input data (geological, lithological and hydrological) were collected from databases belonging to the studied region and for specific coefficients used to simulate the evolution of pollutant concentrations were consulted specialized papers developed for similar areas from a structural point of view.

4. Results and discussions
The spatial and temporal evolution of pollutants in the unsaturated area was based on a scenario of accidental pollution with petroleum products, resulting from a storage tank (gasoline/diesel) of a fuel distribution station. The scenario involves the unintentional spillage of petroleum products over six...
months in the first layer of the soil profile (Figure 4). The concentration of benzene accidentally spilt is 50 ug benzene per cm² of soil without a natural load of benzene in the ground.

One-dimensional flow modelling and transport of contaminants in the unsaturated area was performed with the Unsat application, for a single dominant lithological texture in a section of the stratigraphic plane. The studied profile of the unsaturated zone is located near the fuel distribution station, and the lithological texture with a majority share is sandstone.

![Lithological profile in the area of the fuel distribution station](image)

**Figure 4.** Lithological profile in the area of the fuel distribution station

To estimate the evolution of benzene concentration in the unsaturated area, the SESOIL model was used, which simultaneously determines the transport of water, sediments and pollutants in the lithological profile, based on diffusion, adsorption, volatilization, biodegradation, cation exchange and hydrolysis [3]. The model contains three submodels that mathematically model the transport of contaminants, the movement of soil water and soil erosion. The SESOIL model can also simulate seasonal climatic variations and the different properties of the soil with the depth of the studied lithological profile.

In the studied profile, the transport of contaminants was modelled with simulated biodegradation as a process with the modelled decomposition of first-order substances. The transport of benzene in the unsaturated area was carried out for 20 years from the beginning of the pollution of the first layer (the area of fuel tanks) and the climatic data for the simulated period were imported from the Petrosani meteorological station.

The mode of transport of pollutants in the lithological profile was performed without sediment entrainment (suffusion, erosion) with a self-purification capacity of the cover formations for fissure or karst environments determined using the Bolsenkotter method. Modelling the transport of contaminants
in the unsaturated area requires knowledge of the physical and chemical properties of the aquifer (Table 2) because it interacts with the unsaturated area (muddy) through capillary phenomena.

| Groundwater settings                  | Value | Unit   |
|--------------------------------------|-------|--------|
| Saturated Hydraulic Conductivity     | 76    | cm/ day|
| Hydraulic gradient                   | 0.056 | -      |
| Thickness of saturated zone          | 15    | m      |
| Width of contaminate zone            | 2     | m      |
| Background concentration             | 0     | mg/l   |

Table 2. Characteristic parameters of the aquifer

The model allows the evaluation of the potential concentration of the contaminant in the groundwater or the saturation zone, placed below the contaminated area, this estimate does not take into account the dynamics of the transformation of the contaminant into the aquifer. The extension of the benzene concentration in the ford area (Figure 5) is represented by the variation of the pollutant depth with time.

![Figure 5](image)

**Figure 5.** The expansion of the pollutant concentration in depth

The expansion of the concentration is strictly increasing until the last year of the simulation, which underlines the need for the early start of the practices of remediation of the subsoil and final removal of the pollutant. If the contaminant is leached into the lower layers of the unsaturated zone, the rehabilitation of groundwater quality must be achieved by alternatively combating soil and groundwater pollution. The risk of contamination of the saturated area (aquifer) increases with the maximum depth of leaching of benzene, due to the seasonal variation of the hydrostatic level. The penetration of the pollutant to the capillary zone favours the transfer of contaminants in the aquifer, limiting the use of the water resource to its maximum potential.

The magnitude of benzene in the unsaturated area (Figure 6) represents a distribution of the concentration of benzene in the soil profile and its variation over time (20 years in our case). Information on the concentration of benzene in the soil allows the choice of the most efficient methods for depollution of lithological layers.
Figure 6. Benzene concentration in soil moisture

The distribution of the pollutant concentration in the modelled lithological profile indicates an increase in the degree of pollution of the unsaturated area in the lower layers over time. If in year one benzene pollution was predominant only in the upper layers after a period of 10 years it manifests itself in depth where it tends to accumulate in the lower part of the unsaturated area.

Depollution of the soil with petroleum products and their removal from the mineral matrix can be done simultaneously with the purification of water from the unsaturated area. Water purification can be done by pumping contaminated water to a treatment plant that recirculates it back to the aquifer after depollution [6, 8].

From the risk assessment point of view, the contamination of aquifers, the increase in concentration can be quantified as a probability of pollutant transfer and provides information on the area of influence of the pollutant. In contrast, the magnitude can be quantified as the severity of an adverse event which have been placed on the other site.

5. Conclusions
Research conducted in the central part of Hunedoara County emphasizes the importance of groundwater protection because the process of industrialization of society requires the development of new economic activities that emit or discharge into the environment new harmful substances with unknown effects on terrestrial ecosystems.

The temporal and spatial evolution of petroleum products in the ford area differs from a regional and local point of view depending on the lithological typology and the seasonal variation. Evolution of
contaminants in the vadose zone, in case of surface pollution, is manifested by the displacement of the pollutant towards the lower layers of the lithological profile.

Understanding the evolution of the pollutant concentration in the studied soil profile provides essential information for choosing methods for soil and groundwater depollution, such screening is useful to see the degree of pollution of the unsaturated area and to investigate lithological textures in terms of distribution and of rock volumes. In addition to the modelling of petroleum products, the greased application also allows the modelling of pesticides and substances obtained from unsustainable agricultural practices, runoff from landfills and the behaviour of volatile organic compounds.

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