VULNERABILITY TO POLLUTION OF PHREATIC AQUIFERS IN THE AREA OF THE GREEN SCHISTS OF THE CENTRAL DOBROGEA MASSIF. CASE STUDY: FÂNTÂNELE, CONSTANŢA COUNTY

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Abstract. The assessment of the level of groundwater protection, formalized by the expression "vulnerability to pollution of aquifers", frequently used since 1980, still faces the problem of identifying a representative index (e.g. DRASTIC, GOD, SINTACS, EPIK, etc.), an index that must reflect the complex characteristics of hydrostructures and contaminants. In order to assess the vulnerability to pollution of phreatic aquifers, a 4D model has been developed, a model that integrates the 3D features of the hydrostructure and time, the fourth dimension of the model. The proposed model is applied for a phreatic aquifer from the arid area of south-eastern Romania. The phreatic aquifers, in the green-schists area of the Central Dobrogea Massif, are accumulated in loessoid deposits with heterogeneous particle size composition and in the altered area of green-schists. These low-resource aquifers are "protected" by a vadose zone with variable thickness, whose transport capacity is determined by the moisture resulting from the precipitation regime. The vulnerability of the phreatic aquifer to pollution is synthesized as the time required for a contaminant to cross the vadose zone (in short: duration time of pass over), the relevant vulnerability index that integrates the characteristics of the vadose zone (thickness, particle size composition, lithology and moisture) and of contaminants.

Keywords: vulnerability to pollution, vadose zone/unsaturated zone, duration time of pass over.

Rezumat. Vulnerabilitatea la poluare a acviferelor freatice din zona șisturilor verzi din Masivul Central-Dobrogean. Studiu de caz: Fântânele, județul Constanța. Evaluarea nivelului de protecție a apelor subterane, formalizată prin expresia „vulnerabilitatea la poluare a acviferelor" și folosită frecvent începând din anul 1980, se confruntă și astăzi cu problema validității unui index unic reprezentativ (ex. DRASTIC, GOD, SINTACS, EPIK etc.), un indice care trebuie să reflecte caracteristicile complexe ale hidrostructurilor și contaminanților. Pentru evaluarea vulnerabilității la poluare a acviferelor freatice a fost elaborat un model 4D, model care integrează caracteristicile 3D ale hidrostructurii și timpul, a patra dimensiune a modelului. Modelul propus se aplică pentru un acvifer freatic din zona aridă a sud-estului României. Acviferele freatice, din zona șisturilor verzi din Masivul Central Dobrogean, sunt acumulate în depozite loesoide cu compoziție granulometrică eterogenă și în zona alterată de sisturi verzi. Aceste acvifere cu resurse reduse sunt „protejate" de o zona vadoasă cu grosime variabilă a cărei capacitate de transport este determinată de umiditatea rezultată din regimul de precipitații. Vulnerabilitatea la poluare a acviferului freatic este sintetizată ca timpul necesar pentru ca un contaminant să traverseze zona vadoasă (pe scurt: durată de traversare), indice de vulnerabilitate relevant care integrează caracteristicile zonei vadoase (grosime, dimensiunea particulelor, litologie și umiditate) și ale contaminanților.

Cuvinte cheie: vulnerabilitatea la poluare, zonă vadoasă/zonă nesaturată, durată de traversare.

INTRODUCTION

The article proposes a complex 4D model for assessing the vulnerability to pollution of phreatic aquifers from the arid area of southeastern Romania (the green-schists area of the Central Dobrogea Massif). The 4D model includes the 3D model of the hydrostructure, the physico-chemical characteristics of contaminants, and time, as the fourth dimension of the model. The study area (Fântânele, Constanţa County) is investigated by direct methods (boreholes) and indirect methods (vertical electrical sounding profiles) (PESCARU et al., 2020) that provide the data required to achieve a conceptual model of the Fântânele hydrostructure. The migration conditions of the contaminants are completed with the meteorological data, the types of land use, the potential sources of contamination and the types of associated contaminants.

The 4D model synthesizes the vulnerability level of the Fântânele hydrostructure using the time necessary for a contaminant to cross the vadose zone, from the pollution source to the aquifer, duration time of pass over evaluated based on a stochastic-analytical model. The 4D model will be calibrated based on the results of the ongoing monitoring programme for the chemical characteristics of the phreatic aquifer.

METHODOLOGY

The complex 4D model for assessing the level of protection against pollution for phreatic aquifers from the arid area is based on a methodology devoted to: a) analysis of the protection factors of the aquifer, and b) simulation of contaminants migration through the vadose zone of the aquifer. The nalysis of the protection factors of aquifers is based on three geostatistical models: a) indicator kriging for lithology of 3D spatial model of hydrostructure; b) ordinary kriging and conditional simulation for 3D parametrical models (porosity, moisture of vadose zone, concentration of petroleum products, pesticides, heavy metals) of hydrostructure; c) universal kriging that assumes a trending mean for 3D energetic model (piezometric surface of aquifer) of hydrostructure.

In addition to geostatistical models, specific methodologies for processing laboratory samples and for synthesizing geophysical data were used to evaluate the parameters of the vadose zone (moisture, thickness of the unsaturated zone, concentration of contaminants). The data required for the analysis of protection factors were obtained through direct (boreholes) and geophysical (vertical electrical sounding) investigations in the Fântânele area, where the case study was conducted.

The simulation of contaminants migration is based on a stochastic-analytical model integrated in the UnSat Suite Plus application that combines models used for simulating the migration of contaminants in the vadose zone and in the contaminated aquifer. To simulate the transfer of contaminants in the vadose zone, for long time intervals, the following was selected: *a hydrological model* to evaluate: a) the average moisture of the vadose zone, as a ratio between the restoration of moisture and the thickness of the vadose zone; b) the hydraulic conductivity of the vadose zone depending on the water pressure in the pores, the pore discontinuity index and the permeability of the mineral matrix and c) the velocity of groundwater flow in the vadose zone and *a contamination model* for: a) partitioning the contaminant between solid, liquid and gaseous states, and b) upward (volatilization) and downward contaminant migration (advection, sorption, ion exchange, biodegradation and hydrolysis) (SEDRATI et al., 2018). *The erosion model*, useful when the source of pollution is on the land surface, *is neglected* because in the study area contaminants are identified in the soil at depths between 0.20 and 1.0 m, a depth at which the effect of erosion is totally insignificant.

The synthetic parameter of simulating the migration of contaminants of various species is the time period of pass over the vadose zone, used like a cumulative index of aquifer vulnerability.

INVESTIGATION OF SITE

The study area is located in the perimeter of the Fântânele Commune in the Constanţa County, located in the Central Dobrogean Massif. The Central-Dobrogean Massif is positioned in the middle part of Dobrogea, being bordered to the south by the Palazu Fault, and to the north by the Peceneaga-Camena Fault. The administrative territory of the Cogealac and Fantanele Communes is located in the northeastern part of Constanța County, at approx. 50 km from the Constanța City on the 22 National Road Constanța - Mihai Viteazu - Tulcea. The object of the study in the investigated area is the formation of green schists of Proterozoic age and sedimentary formations of Quaternary age (MUTIHAC et al., 1990).

The green schist formation appears on the surface of the ground but also in depth covered by loess and loessoid deposits. Green schists are impermeable geological formations so they do not circulate or store water. Altered and cracked zones at the surface of the land were excluded. Sedimentary formations are represented by loess, deposited following wind sedimentation over the of green schists formations. They are usually silty, porous and unconsolidated with colors ranging from yellow to reddish-yellow. Clay and sandy areas, as well as portions of paleosols, may be present along their entire extent. The Quaternary sedimentary formations are the alluvium deposited by the Fântânele River.

The objectives of the site investigation were: a) soil contamination, b) granulometric composition of the vadose zone, c) moisture of the vadose zone and d) thickness of the vadose zone.

Soil contamination. The simulation of contaminant migration was based on soil testing to a depth of 1m, in 17 points, placed in the vicinity of potential sources of contamination (inhabited area near S1, S3, S4, S6, S7, S8, S10÷S15 points and zootechnical farm near S16÷S20 points (Fig. 1). The total content of petroleum hydrocarbons (TPH) (Table 1) was determined in 17 samples.

Table 1. TPH (mg/g) in soil up to 2m depth (Fântânele area).

Sample	X (m)	Y (m)	TPH (mg/g)	Benzene (mg/g)
S1	783677	351883	0.1211	0.00061
S3	784307	351883	0.1214	0.00061
S4	783677	351703	0.1266	0.00063
S6	784274	351724	0.1213	0.00061
S7	783286	351585	0.1211	0.00061
S8	783684	351564	0.1304	0.00065
S10	783750	351385	0.1227	0.00061
S11	783471	351371	0.1300	0.00065
S12	783074	351364	0.1188	0.00059
S13	783259	351177	0.1224	0.00061
S14	783471	350976	0.1185	0.00059
S15	783690	351177	0.1211	0.00061
S16	783279	349939	0.1478	0.00074
S17	783491	349946	0.1518	0.00076
S18	783399	349787	0.1572	0.00079
S19	783312	349634	0.1503	0.00075
S20	783505	349621	0.1479	0.00074

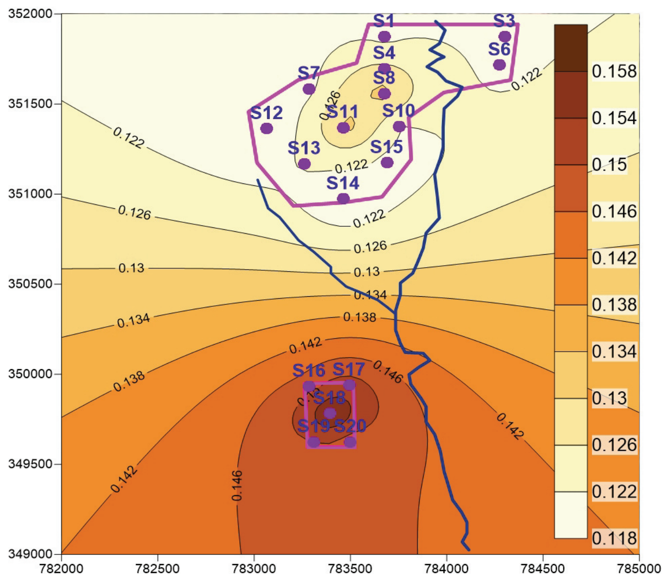

Figure 1. TPH (mg/g) in soil (up to 1m depth; Fântânele).

Granulometric composition of the vadose zone. For the granulometric composition 26 samples from 8 points were collected, at different depths (ground surface, 1m, 2m and 3m) (Fig.1), namely: S22, S27, S31 and S33 - 4 samples, S25 - 3 samples, S28 - 2 samples, S29 - one sample. Samples were taken with a manual drill up to a maximum depth of 3 m. Nine representative samples were selected to determine the particle size composition of the vadose area (Fig. 2).

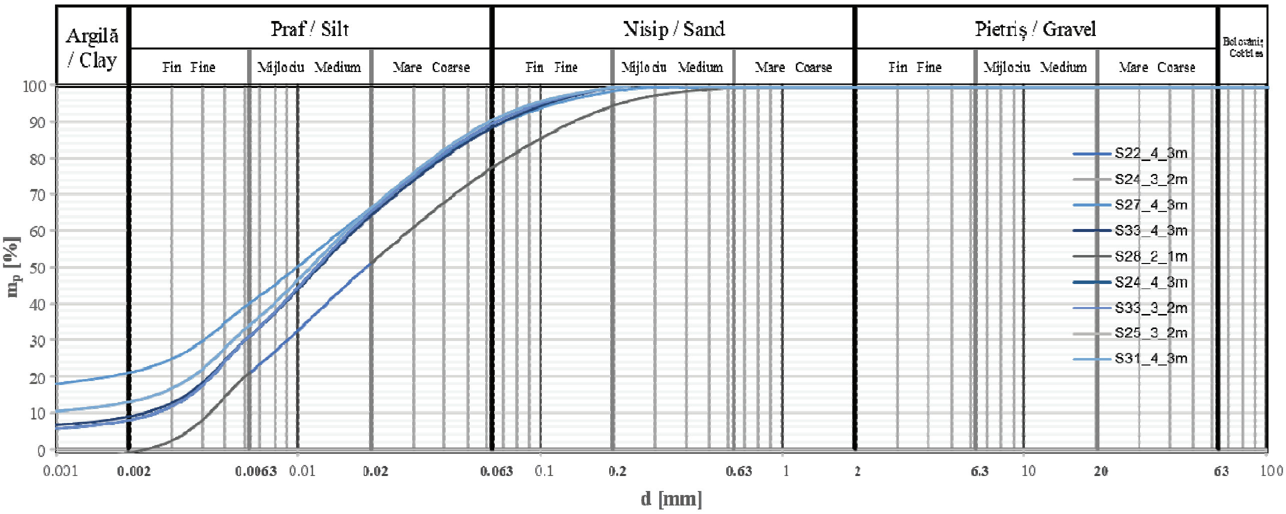

Figure 2. The granulometric composition of the loess from the Fântânele area.

The lithology of the vadose zone, with thicknesses between 2 m and 7 m, is represented by loess, a mobile unconsolidated rock, formed during the Quaternary. The loess is a heterogeneous formation, predominating particles with Ø of 0.005 – 0.01 mm (generally exceeds 50%), the coarse fraction (Ø > 0.2 mm) is missing or is present in insignificant quantities. Regarding the clay content (Ø < 0.002 mm) it is between 15 and 30%. Without an obvious stratification, the loess has a high total porosity (45 – 50%) with tubular pores with predominant vertical orientation.

Table 2. Determination of moisture in the laboratory.

Code	Depth (m)	Sample Conductivity (dS/m)	Resistivity of the sample (ohmm)	Water conductivity at 20°C (dS/m)	Water resistivity at 20°C (ohmm)	TDS NaCl at 20°C (mg/l)	Test temperature (°C)	Suction potential (kPa) +/- 20%	Moisture (%) +/- 4%
S22	0	0.220	45.45	2.420	4.13	1549	27.1	-25.25	24.3
	1	0.026	433.33	0.740	13.51	474	26.3	-85.82	15.0
	2	0.170	58.82	2.290	4.37	1466	26.5	-114.81	22.1
	3	0.420	24.02	3.270	3.06	2093	27.2	-60.54	28.4
S24	0	0.159	62.89	2.720	3.68	1741	26.9	-106.92	19.9
	1	0.030	333.33	1.180	8.47	755	27.0	-42.15	14.7
	2	0.157	63.69	3.500	2.86	2240	27.0	-111.99	17.5
	3	0.230	43.48	3.470	2.88	2221	27.0	-22.80	19.8
S25	0	0.180	55.56	2.900	3.45	1856	27.0	-87.35	20.4
	1	0.012	833.33	0.326	30.67	209	27.2	-118.25	15.6
	2	0.021	476.19	0.945	10.58	605	27.5	-179.83	13.9
S27	0	0.209	47.85	2.585	3.87	1654	26.9	-37.39	23.1
	1	0.068	147.06	0.950	10.53	608	27.3	-66.78	17.3
	2	0.040	250.00	1.667	6.00	1067	27.1	-59.74	14.4
	3	0.030	333.33	0.876	11.42	561	27.2	-37.31	16.1
S28	0	0.090	111.11	2.490	4.02	1594	27.0	-56.51	16.4
	1	0.030	333.33	1.290	7.75	826	27.1	-130.37	14.3
S29	0	0.192	52.08	2.183	4.58	1397	25.8	-98.08	24.0
S31	0	0.090	111.11	1.354	7.39	867	27.2	-36.89	21.0
	1	0.101	99.01	1.631	6.13	1044	27.1	-123.88	20.3
	2	0.012	833.33	0.225	44.44	144	27.3	-23.50	17.6
	3	0.010	1000.00	0.472	21.19	302	27.5	-63.21	14.0
S33	0	0.160	62.50	3.020	3.31	1933	27.1	-59.52	19.0
	1	0.100	100.00	3.160	3.16	2022	26.9	-27.55	15.7
	2	0.115	86.96	4.101	2.44	2625	27.4	-38.19	14.9
	3	0.060	166.67	0.460	21.74	294	27.1	-27.69	29.2

Quartz predominates in the mineralogical composition (60 - 70%), followed by feldspar, pyroxene, clay minerals, etc. Loess has a good permeability with significant variations from one area to another; for this reason, three categories of loess were selected to simulate the migration of specific contaminants: sand - clay silt (SCS), clay silt (CS) and silt (S).

Moisture of the vadose zone. The high moisture of the permeable terrain favors the contaminants migration, their maximum migration velocity reaching the saturation state of the permeable material. The Fântânele hydrostructure has a loessoid vadose zone with thicknesses between 2 and 7 m. In order to evaluate the real moisture at the upper part of the vadose zone, 26 samples from 8 investigation points were collected (Fig. 1; Table 2). Sampling was performed with a manual drill up to a maximum depth of 3 m in 06/19/2018.

Moisture determination was performed with MPS-1 and 5TE Dielectric Water Potential Sensor. The average moisture value for the 26 soil samples is 18.80% with an average estimation error of 4% (Table 2).

Thickness of the vadose zone. The 3D spatial model of the hydrostructure (Fig. 3) that evaluates the spatial variability of the thickness of the vadose zone and of the aquifer in the Fântânele area was made using indicator kriging with data obtained from 17VES (Table 3).

Table 3. Data used for the 3D model of the Fântânele hydrostructure.

Nr. crt.	Moni-toring station	X (m)	Y (m)	Thickness of the vadose zone (m)	Aquifer thickness (m)	Land elevation Z (m)
1	S1	783676.41	351873.51	5.53	6.43	114.46
2	S3	784300.16	351873.51	6.84	3.52	114.66
3	S4	783676.41	351697.09	5.09	6.82	113.42
4	S6	784274.96	351715.99	6.71	3.17	114.07
5	S7	783285.78	351583.68	4.71	9.04	114.46
6	S8	783676.41	351558.48	4.67	7.25	112.53
7	S10	783752.02	351375.77	4.08	6.76	110.28
8	S11	783462.20	351369.47	4.17	10.69	112.68
9	S12	783065.27	351363.17	4.49	9.20	114.43
10	S13	783260.58	351167.85	4.13	12.18	112.89
11	S14	783462.20	350972.54	3.34	19.48	112.07
12	S15	783689.01	351174.15	3.56	9.10	107.70
13	S16	783285.78	349932.96	2.03	0.90	108.04
14	S17	783493.70	349939.26	6.53	0.46	96.28
15	S18	783392.89	349781.74	4.33	0.74	103.26
16	S19	783310.99	349624.23	3.87	3.34	108.40
17	S20	783500.00	349624.23	2.66	0.75	103.29

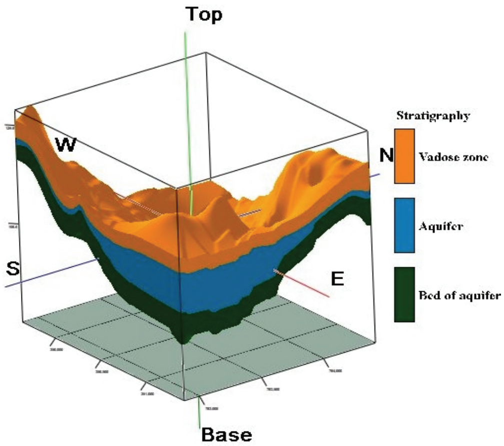

Figure 3. 3D model of the hydrostructure.

RESULTS

The 4D model integrates the spatial, parametric and hydrodynamic environment of the conceptual model of the Fântânele hydrostructure, using time to pass over the vadose zone as the fourth dimension.

To assess the pollution vulnerability of the phreatic aquifer, the contamination of the aquifer with three categories of contaminants was simulated: benzene, the most mobile constituent that can be found associated with TPH in oil complex mixtures, pesticides (DDT, Pyrene, Dieldrin), heavy metals (lead). In a typical crude oil one can find TPH (95%), Benzene (0.5%), PAH (0.7%) and others in certain percentages. If, for example, we have a TPH of 1000 mg / kg representing 95%, then the associated benzene could be a maximum of 5 mg/kg. The concentration of benzene from which the simulation starts is about 200 times lower than the concentration of TPH with which it can be associated.

The simulation of the aquifer contamination was performed on the 17 profiles (Fig. 1) with three different lithological types existing in the Fântânele area: sand-clay silt (SCS), clay silt (CS) and silt (S). The results of the simulation are intended to assess the vulnerability to pollution of the aquifer according to the type of contaminant, lithology and thickness of the vadose zone.

For benzene, pesticides and heavy metals, the contamination of the vadose zone over time indicates significant differences due to the different degree of absorption of the three lithological types (SCS, CS and S). Benzene, with maximum mobility, is distributed over the entire thickness of the vadose zone with variable concentrations, depending on the particle size composition of the loess (Table 4).

Pesticides and lead are fixed on the mineral matrix in the first 15 centimeters of the vadose zone with variable concentrations (Table 5). The simulation of benzene migration on the S6 profile highlights the effect of lithology on the distribution of benzene concentration in the vadose zone, with direct effects on the benzene concentration reached in the phreatic aquifer placed below the vadose zone. For sand-clay silt, clay silt and silt, lithologies dominated in the Fântânele area, the clay component retains benzene in the vadose area reducing aquifer contamination (Fig. 4).

The effect of lithology, correlated with the variation of the vadose zone thickness and the initial benzene concentration at the beginning of the 20-year simulation period, leads to significant variations in the duration time of pass over and the benzene concentration reached in the aquifer (Fig. 5 and Table 6).

The spatial distribution of the time required for benzene to cross the vadose zone is proposed as a graphic form to express the vulnerability of the aquifer to benzene contamination. The minimum time to cross the vadose zone (3 years) indicates a maximum vulnerability of the aquifer in the S20 profile area and the maximum duration required for benzene to cross the vadose zone (12 years) indicates a minimum vulnerability in the S17 profile area (Fig. 6).

For the 17 profiles from the Fântânele area, the results of the simulation for benzene (Table 6; Fig. 7) indicates a linear correlation between the time period of pass over (Tmin) and the thickness of the vadose zone (TVZ): Tmin = 1.658xTVZ + 1.154, with a Pearson coefficient = 0.5819. The duration of pass over the vadose zone (Tmin) represents the time required for the vertical migration of the contaminant (benzene in the case of the study) from the source of contamination to the aquifer and reaching a minimum concentration of benzene in the water of aquifer, 0.15 mg/liter for the performed study.

If we analyse the correlation between TVZ and the time of benzene pass over for the maximum concentration of benzene in the water of aquifer (Tmax) we find a linear correlation of lower intensity (Pearson coefficient 0.2207) affected by the parametric features of each profile, over a longer migration period (Fig. 7).

Table 4. The results of simulating the migration of benzene in the study area (S6).

Depth (m)	Benzene concentration (T=20 years) x200 (microgram/kg)		
	SCS	CS	S
0.13	0.00	0.00	0.00
1.48	0.00	0.01	0.00
1.67	0.00	0.01	0.02
1.86	0.00	0.02	0.09
2.05	0.00	0.03	0.39
2.24	0.00	0.05	1.43
2.43	0.00	0.09	4.27
2.62	0.00	0.16	10.67
2.81	0.00	0.29	22.47
3.00	0.00	0.54	40.41
3.19	0.00	1.07	62.91
3.38	0.00	2.21	86.04
3.57	0.00	4.84	104.80
3.76	0.00	11.38	115.17
3.95	0.00	28.33	114.98
4.14	0.00	70.90	103.94
4.33	0.00	164.88	83.56
4.52	0.00	329.64	56.97
4.71	0.00	515.11	21.01
4.90	0.00	0.00	0.00
6.61	3.61	0.00	0.00

Table 5. Results of pesticide and lead migration simulation in the study area (profile S6).

Contaminant	Concentration (T=20 years) [microgram/kg]		
	SCS	CS	S
DDT	0.29	52.51	7.29
Pyrene	16.87	93.70	48.76
Dieldrin	277.03	478.03	477.55
Lead	48.76	478.20	478.20

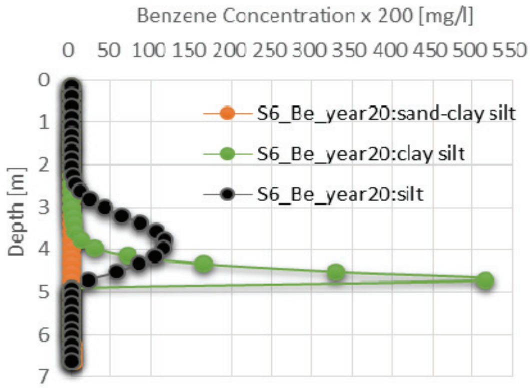

Figure 4. Var. of Be concentration in vadose zone (profile S6) for SCS, CS and S for the 20th years.

Table 6. Time variation of the benzene concentration (x200) reached the aquifer during the simulation (20 years) in 17 profiles.

TIME year	S3_ BE [mg/l]	S1_ BE [mg/l]	S4_ BE [mg/l]	S6_ BE [mg/l]	S7_ BE [mg/l]	S8_ BE [mg/l]	S10_ BE [mg/l]	S11_ BE [mg/l]	S12_ BE [mg/l]	S13_ BE [mg/l]	S14_ BE [mg/l]	S15_ BE [mg/l]	S16_ BE [mg/l]	S17_ BE [mg/l	S18_ BE [mg/l]	S19_ BE [mg/l]	S20_ BE [mg/l]
1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
2	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
3	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.33
4	0	0	0	0	0	0	0	0	0	0	0	0	0.34	0	0	0	1.59
5	0	0	0	0	0	0	0	0	0	0	0	0	1.09	0	0	0	2.36
6	0	0	0	0	0	0	0.81	0.65	0.15	0.76	0	0	1.68	0	0	0	3.38
7	0	0	0.64	0	0	1.05	1.31	0.28	1.20	1.35	0.49	0.47	2.12	0	0	0.16	4.43
8	0	0.99	1.19	0.54	0	1.30	1.50	1.48	1.45	1.57	0.52	0.63	2.29	0	0.22	0.70	5.15
9	0.24	1.44	1.66	1.33	0.60	1.82	2.15	2.11	2.00	2.21	0.74	0.89	3.41	0	1.05	0.98	6.64
10	1.19	1.79	2.03	1.64	1.07	2.22	2.60	2.56	2.44	2.69	0.88	1.05	4.06	0	1.27	1.16	7.74
11	1.52	2.11	2.38	1.93	1.24	2.60	2.99	2.96	2.85	3.10	1.01	1.20	4.41	0	1.46	1.31	7.86
12	1.83	2.48	2.77	2.26	1.40	3.00	3.29	3.35	3.26	3.46	1.12	1.35	4.82	0.31	1.66	1.47	2.44
13	2.07	2.74	3.01	2.53	1.52	3.20	3.03	3.38	3.38	3.36	1.06	1.34	4.53	0.98	1.82	1.53	0.00
14	2.29	2.98	3.21	2.78	1.61	3.38	2.15	3.17	3.27	2.70	1.17	1.45	2.38	1.09	1.94	1.63	0.00
15	2.56	3.28	3.37	3.10	1.81	3.43	0.53	2.04	2.39	1.00	1.41	1.72	0.07	1.22	2.18	1.88	0.00
16	2.79	3.31	2.91	3.37	1.93	2.57	0.01	0.39	0.71	0.04	1.40	1.73	0.00	1.31	2.34	1.94	0.00
17	3.05	3.05	1.68	3.69	2.12	0.94	0.00	0.00	0.02	0.00	1.51	1.90	0.00	1.43	2.57	2.12	0.00
18	3.34	1.60	0.23	4.11	2.65	0.05	0.00	0.00	0.00	0.00	2.45	2.88	0.00	1.68	3.15	2.86	0.00
19	3.16	0.15	0.00	4.04	2.58	0.00	0.00	0.00	0.00	0.00	1.61	2.20	0.00	1.72	3.13	2.13	0.00
20	2.73	0.00	0.00	3.69	2.74	0.00	0.00	0.00	0.00	0.00	1.36	2.23	0.00	1.83	3.33	1.61	0.00

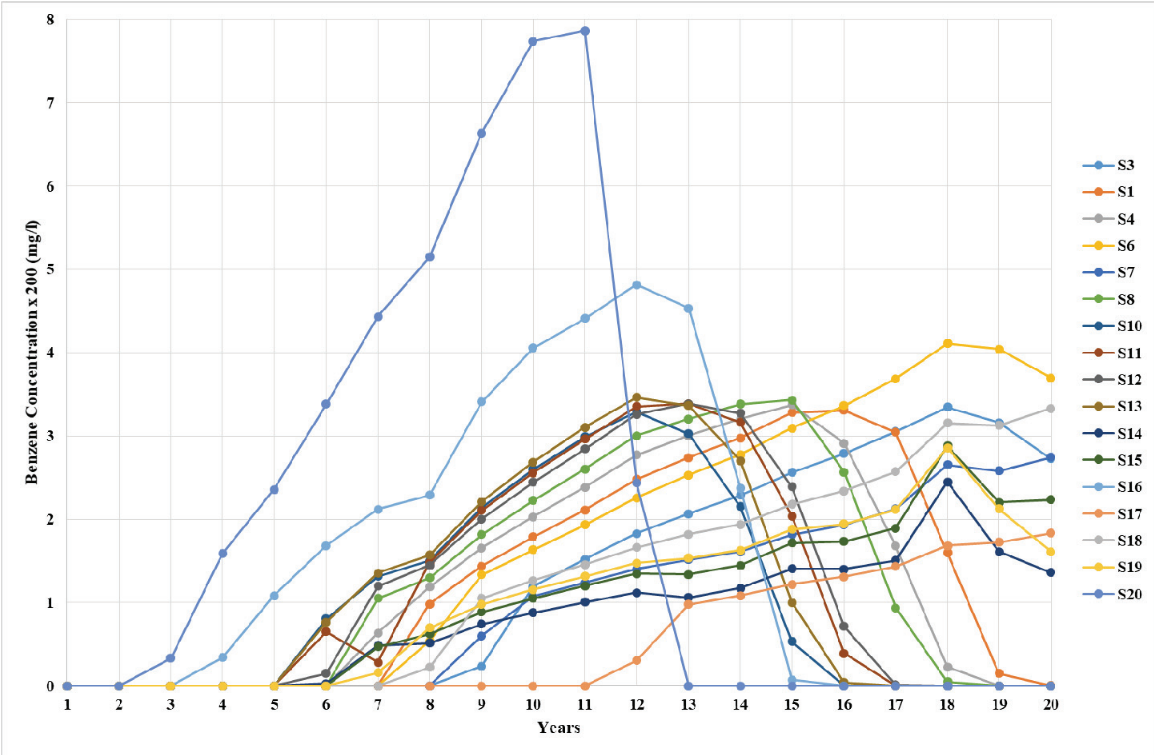

Figure 5. The concentrations of benzene reached in the aquifer during 20 years (17 simulation profiles in Fântânele area).

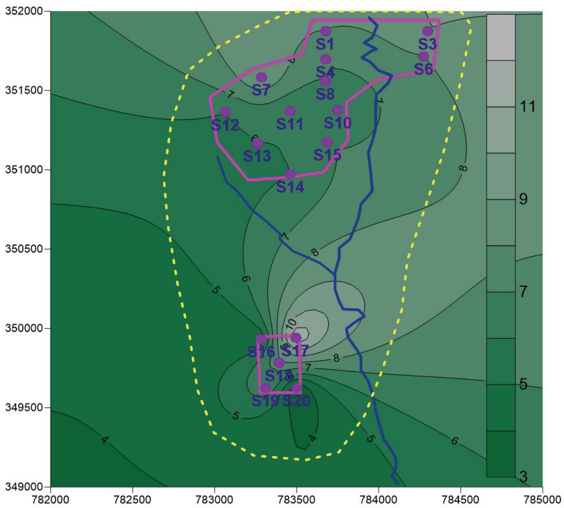

Figure 6. Spatial distribution of the crossing time of the vadose zone.

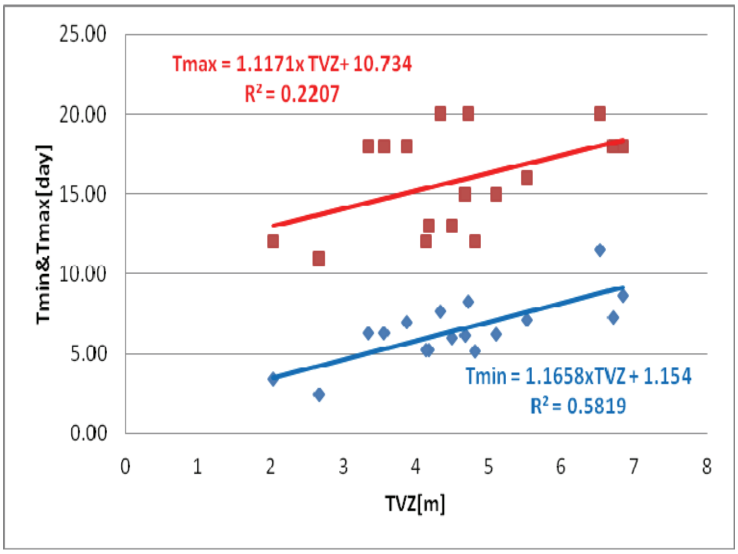

Figure 7. Correlation Tmin/Tmax =f(TVZ) for benzene in the Fântânele hydrostructure.

CONCLUSIONS

The proposed 4D model (X, Y, Z, T) for assessing the vulnerability to pollution of the phreatic aquifer in the Fântânele area consists of conceptual 3D model (X, Y, Z spatial coordinates) of the hydrostructure which includes the spatial, parametric and hydrodynamic model of the Fântânele hydrostructure and 1D non-stationary model (T-time) for contaminant migration in the vadose zone of the phreatic aquifer placed below the vadose zone.

The non-stationary 4D model for assessing the vulnerability to pollution of the Fântânele aquifer takes into account three conditional factors: the thickness of the vadose zone, the lithology of the vadose zone, and the type of contaminant.

The spatial, parametric and hydrodynamic characteristics of the hydrostructure Fântânele are obtained by direct methods (meteorological measurements, laboratory analyses of soil samples taken from boreholes. The data processing was finalized in a 3D complete conceptual model, adequate to simulate the potential contaminants associated with the contamination sources represented by the inhabited area and the zootechnical farm.

The integration of the simulation results of the three categories of contaminants (TPH-benzene, pesticides and heavy metals) in the spatial, parametric and hydrodynamic environment of the hydrostructure Fântânele allowed zoning the vulnerability to pollution based on the time-transfer of contaminants from soil to aquifer.

The results obtained with the 4D model (Table 7) reflect the effect of the two sources of pollution in the investigated area (inhabited area in NNW and zootechnical farm in SW, Figs. 8, 9) using the time of pass over of the vadose zone, in two variants regarding the concentration of benzene reached in the phreatic aquifer:

Table 7. Synthesis of the results of the Fântânele hydrostructure vulnerability assessment.

Proof points	X	Y	TVZ [m]	TPH [mg/g]	Tmin [year]	ConcBEmin (X2000) [mg/l]	Tmax [year]	concBEmax (X200) [mg/l]
S1	783676	351874	5.53	0.1208	7.15	0.99	16	3.31
S3	784300	351874	6.84	0.1214	8.63	0.24	18	3.34
S4	783676	351697	5.09	0.1265	6.23	0.64	15	3.37
S6	784275	351716	6.71	0.1213	7.28	0.54	18	4.11
S7	783286	351584	4.71	0.1207	8.25	0.60	20	2.74
S8	783676	351558	4.67	0.1314	6.14	1.05	15	3.43
S10	783752	351376	4.8	0.1218	5.19	0.81	12	3.29
S11	783462	351369	4.17	0.1312	5.23	0.65	13	3.38
S12	783065	351363	4.49	0.1183	6.00	0.15	13	3.38
S13	783261	351168	4.13	0.1224	5.20	0.76	12	3.46
S14	783462	350973	3.34	0.1181	6.31	0.49	18	2.45
S15	783689	351174	3.56	0.1210	6.32	0.47	18	2.88
S16	783286	349933	2.03	0.1478	3.44	0.34	12	4.82
S17	783494	349939	6.53	0.1523	11.48	0.31	20	1.83
S18	783393	349782	4.33	0.1584	7.68	0.22	20	3.33
S19	783311	349624	3.87	0.1505	6.94	0.16	19	2.86
S20	783500	349624	2.66	0.1484	2.45	0.33	11	7.86

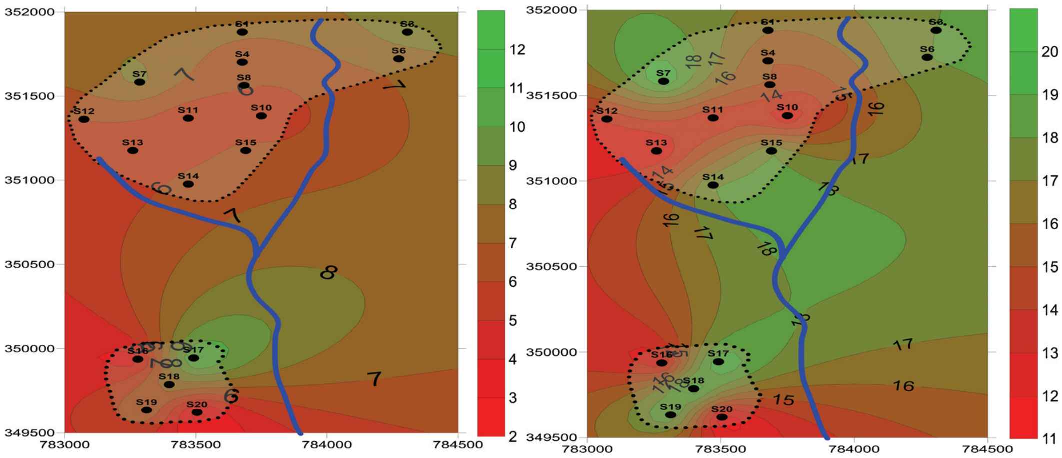

Figure 8. Distribution of duration time of pass over the vadose zone (Tmin. and T max [years]) for the Fântânele hydrostructure.

a) Tmin: time period of pass over the vadose zone of benzene, from the ground until a minimum concentration of benzene is recorded in the aquifer water (minimum concentration that signals pollution for the hydrostructure: ConcBEmin = 0.15 mg/liter registered on profile S12 at Tmin = 6 years from the start of the pollution process simulation);

b) Tmax: time period of pass over vadose zone of benzene, from the ground until a maximum concentration of benzene is recorded in the aquifer water (ConcBEmax = 3.38 mg/liter, registered on profile S12 at Tmax=13 years from the start of the pollution process simulation).

Assuming that the migration processes of contaminants on the verticals of the 17 profiles are quasi-independent, the 2D models built for the distribution of the Tmin and Tmax (from Table 7) indicate a maximum vulnerability to pollution in the vicinity of the inhabited area in NNV and the zootechnical farm in SW.

The configuration of the areas of maximum vulnerability does not significantly differ for the two variants of calculation for the period of pass over (T min and T max), confirming the fact that the main role in the evaluation of the time period of pass over is held by the thickness of the vadose zone (TVZ). The correlations between time period of pass over and minimum/maximum concentrations of benzene in groundwater are of low intensity (Fig. 9).

The proposed 4D model, compared to the classical model for assessing the vulnerability to aquifers pollution (SAHA & ALAM, 2014; CHENINI et al., 2015; KAZAKIS et al., 2015; KUNAR & KHRISMA, 2019; BĂRBULESCU, 2020; BOUMAIZA et al., 2021) is a dynamic non-stationary model, calibrate using the characteristics of the contaminant and the spatial, parametric and hydrodynamic characteristics of the hydrostructure. The static interpretation of the parameters of the contamination sources, characteristics of the vadose zone and the aquifer does not allow for the correct assessment of the vulnerability to pollution of a hydrostructure in their real dynamics.

The design of methods for the protection and remediation of groundwater quality in the aquifers from the Dobrogea Central Massif is conditioned only through knowledge of the vulnerability to pollution caused by climate regime, the characteristics of vadose zone and types of contaminants from pollution sources. Over the 20-year simulation period, humidity has a seasonal variability that was estimated based on meteorological data from the Jurilovca station using the annual balance model.

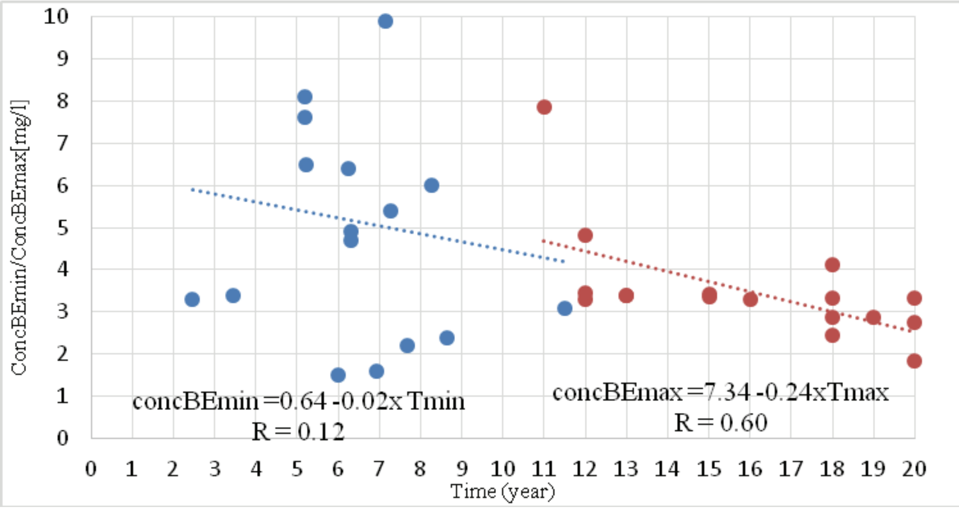

Figure 9. Correlations between benzene concentrations in aquifer and time of pass over vadose zone.

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