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ESTIMATING THE MOISTURE REGIME IN VARIABLY-SATURATED ARSENIC CONTAMINATED ALLUVIAL SEDIMENTS BY USING HYDRUS-1D WITH DAILY METEOROLOGICAL DATA

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Abstract

As a result of historical mining activities, some layers in the Ogosta Valley`s floodplain sediments are highly enriched in arsenic (As). Reductive release of iron (Fe) and As in the floodplain soil could be expected under reducing conditions, which would lead to an increase of the more toxic As species in the soil pore water. Therefore, it is important to understand whether the vadose zone in the Ogosta’s floodplain is a subject to water saturation during intensive rainfalls. The study provides a model based on the HYDRUS-1D code, along with the mathematical description of processes implemented into, especially those used to estimate the daily evapotranspiration rates and water flow from the soil surface to the groundwater level during ten-days scenarios including intensive rainfalls. The results from the simulations for April and July are compared in order to reveal the moisture regime of the vadose zone in the river floodplain of the Ogosta Valley.

Keywords: *Ogosta Valley, vadose zone, soil water saturation, numerical modelling*

1. INTRODUCTION

Environmental pollution with arsenic (As) is a problem of a global scale, which is a serious concern for 36 countries on 6 continents (Stoyanova and Kotsev, 2016; Rahman et al., 2006). Increased concentrations of As in soil are likely to be registered in river valleys worldwide where ferrous and base-metal ores are extracted and processed (Bird et al., 2010). In such areas, river floodplain is often the most badly affected since the river system is usually the main carrier of the contaminants and acts as second source of pollution during high flood events. The water content in riparian soils is relatively high due to the shallow groundwater table and its intensive dynamics. The soils near the rivers are frequently water-saturated, especially at high river levels or when inundated. Therefore, the vadose zone in the floodplain sediment is affected by variable redox conditions. Being a redox-sensitive element, arsenic undergoes oxic-anoxic cycles of transformation in riparian soil (Parsons et al., 2013). The contaminant can occur in several oxidation states in the environment, although in most natural groundwaters As occurs either as trivalent arsenite [As(III)] or pentavalent arsenate [As(V)] (Panagiotaras et al., 2012). In well-aerated environment the predominant As species are arsenates as $H_2AsO_4^-$ and $HAsO_4^{2-}$, while in anoxic water-saturated soils arsenites as $H_3AsO_3^0$ and $H_2AsO_3^-$ prevail in the soil solution (Smedley and Kinniburgh, 2002). Trivalent As is more toxic and about 50 times less retardable in soil than the pentavalent one in regards to distribution coefficient values (Smedley and Kinniburgh, 2002; Bowell et al., 2014; Fawcett et al., 2015). Arsenic speciation and transport in a medium with variable state of saturation are controlled mainly by the highly varying oxidation-reduction conditions (Bowell et al., 2014; Markelova et al., 2018). It was observed that a moisture saturation of the vadose zone caused by flooding decreases the redox potential, and may lead to rapid change from oxic to anoxic state of the environment (Appelo and Postma, 2005). Thus, reductive release of iron and arsenic in the floodplain soil could be expected under anoxic conditions, which would lead to an increase of the more toxic As (III) species in the soil pore water.

Although there are many investigations dealing with arsenic mobilization in soils during floods (Masscheleyn et al., 1991; Zheng et al., 2004; Weigand et al., 2010; Xu et al., 2017), fewer studies are available on the impact of precipitations above the water saturated zone in arsenic contaminated soils. Because intensive or prolonged rainfalls are common phenomena in many regions worldwide, it is important to understand whether the vadose zone in arsenic contaminated floodplains is a subject to saturation not only by inundation but also by precipitations and infiltration.

In earlier research, one-dimensional modelling scenarios for water flow transport were performed for arsenic contaminated soil profiles in the Ogosta Valley, located in Northwestern Bulgaria. Using the software HYDRUS-1D, it was found that average daily precipitation rates could cause partial or full saturation of some layers of the polluted floodplain sediment, especially at high groundwater levels (Antonov et al., 2018). As a further step, more detailed scenarios for the moisture regime of the local floodplain soils are applied in this study, based on historical daily meteorological data.

2. STUDY AREA

2.1. Ogosta Valley

The Ogosta River runs from the western part of the Balkan Range to the Danube along a distance of 141.1 km. The studied area is located in the upper stretch of the valley near the village of Gavril Genovo with an average altitude of 230 m (Figure 1). The geomorphological forms in the valley floor are represented mostly by the topography of the low floodplain and upper floodplain of the river. Annual average temperature of 10.4 ºC is calculated for the meteorological station Berkovitsa for the period of 1931-1983 (Institute of Hydrology and Meteorology, 1983). It has an altitude of 405 m and is located 22 km southwest of the investigated site. The annual average sum of precipitations at the meteorological station of Montana is 628 mm for the period of 1931-1985 (Koleva and Peneva, 1990). The station is located downstream in the Ogosta Valley 14 km east of the village of Gavril Genovo.

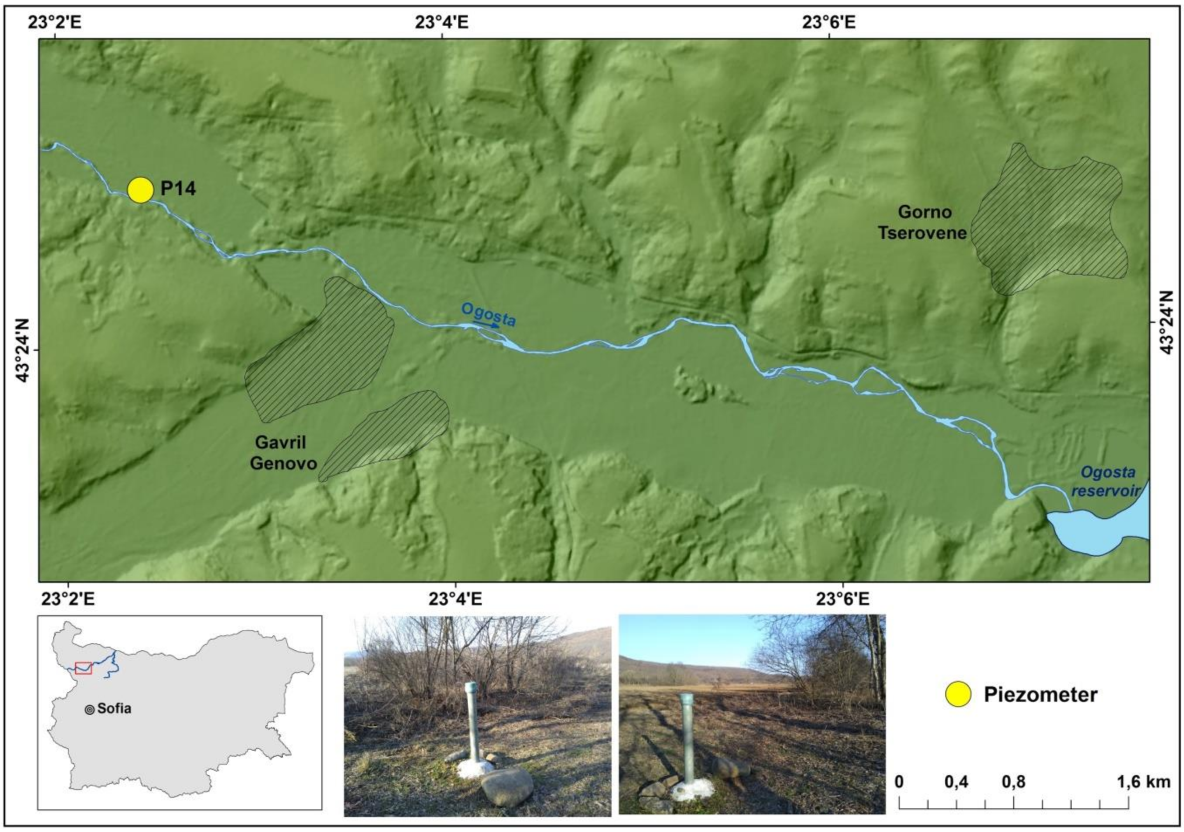

Figure 1. Location of the investigated site P14 in the Ogosta Valley**.**

Over a long period of time, the area of research has been subject to intensified anthropogenization due to extraction and processing of precious metal and base metal ores (Milev et al., 1996). According to the same authors, the ore mining in the upper stretch of the Ogosta River dates back to the time of the Roman Empire during the reign of the Emperor Augustus when the golden sands of the Dalgodelska Ogosta River were processed. Extraction of lead, silver and iron began in the 2nd century AD by the Thracian tribes. Industrial mining activities in the vicinity of the town of Chiprovtsi started in 1951 and ceased in 1999 with a peak in the 60s and 70s of the last century.

2.2. Investigated site

The investigated soil profile of piezometer P-14 is situated in the valley section between the village of Beli Mel and the Ogosta dam lake. It has coordinates 23º3′50.4102″E, 43º24′17.3838″N and is representative for the low floodplain in the valley. The profile is 68 meters away from the river bank where the vertical distance from the ground surface to the river bed is 234 cm (Figure 2). The thickness of the vadose zone is relatively large with a maximum depth of 200 cm. The site of P-14 is characterized as one of the arsenic polluted spots in the Ogosta Valley. The concentration of arsenic in the soil is in the range of 37–856 mg/kg for the six distinctive layers to a depth of 200 cm, coinciding with the vadose zone.

The sediments are built of sand and gravel with silt loam and sandy loam fillings (Figure 3). Official meteorological data for April and July 1965 were used for the ten-day periods of simulations (Table 1).

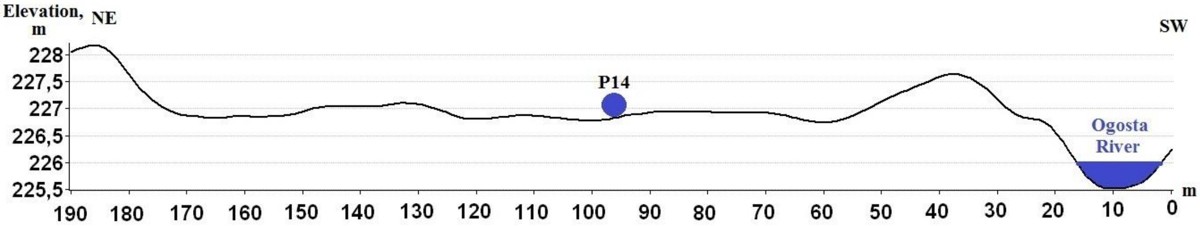

Figure 2. NE-SW cross-section of the left bank of Ogosta Valley with the investigated site P14.

Table 1. Meteorological data used for the simulations

month, year	April, 1965									
Date	9th	10th	11th	12th	13th	14th	15th	16th	17th	18th
Day in the year	99	100	101	102	103	104	105	106	107	108
Rainfall [mm]	0.5	3.4	0.0	5.0	6.4	3.5	11.0	11.0	7.5	0.0
Air temperature, min [˚C]	9.8	8.4	3.0	2.4	0.5	2.0	3.5	4.4	4.5	4.9
Air temperature, max [˚C]	13.5	12.1	8.9	5.7	4.1	4.1	5.4	7.2	6.5	15.1
month, year	July, 1965									
Date	1st	2nd	3th	4th	5th	6th	7th	8th	9th	10th
Day in the year	182	183	184	185	186	187	188	189	190	191
Rainfall [mm]	0.0	2.0	12.4	0.0	0.0	0.9	0.0	0.0	0.0	0.0
Air temperature, min [˚C]	15.4	16.0	15.9	16.4	19.2	15.0	11.1	12.1	19.0	15.6
Air temperature, max [˚C]	29.2	33.1	30.2	29.8	36.5	23.8	25.1	30.0	28.8	26.9

Source: National Institute of Meteorology and Hydrology at Bulgarian Academy of Science

A high flood event occurred in the Ogosta Valley in the mid-April, 1965 following a rainstorm in the region. The rainfall was several times lower in the investigated area compared to the southern high mountains of the Balkan, but still classified as moderate intensive ones ranging within 10–15 mm/day (Koleva and Peneva, 1990; eds. Stanev, Kyuchukova and Lingova, 1991). We assume that precipitations of such intensity are manifested at a sufficient frequency to have significance for the mobilization and transport of arsenic into the soil. Another reason for choosing this period is the presence of rainfall of similar intensity rainfall during early spring and midsummer, which makes it possible to compare results obtained at different air temperatures and evapotranspiration rate.

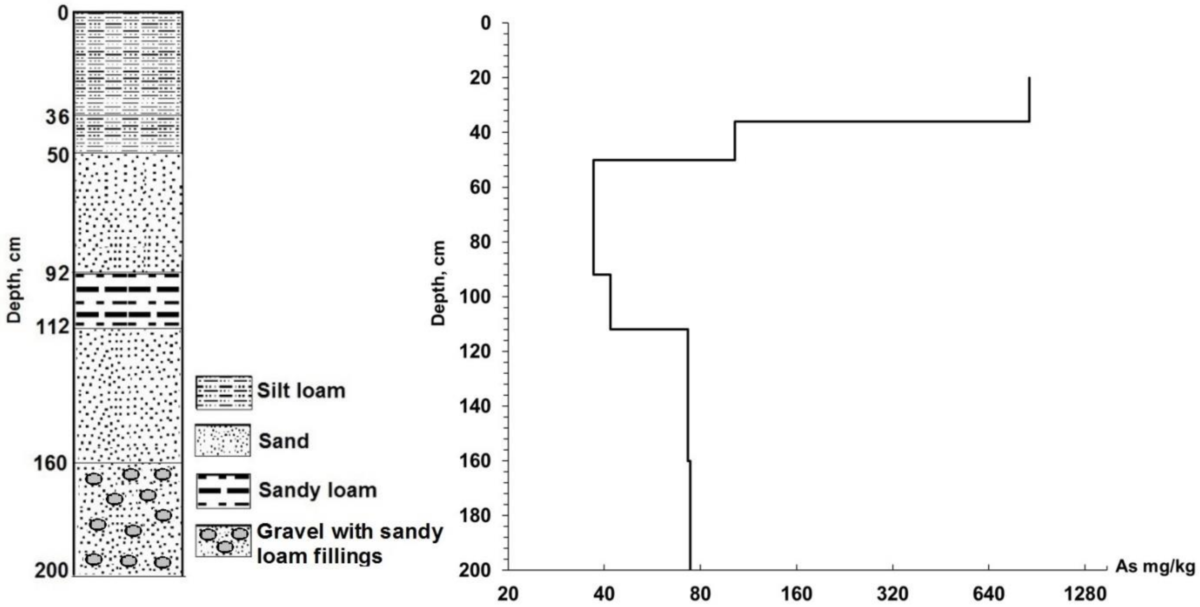

Figure 3. Texture and vertical distribution of the arsenic in depth of the studied soil profile.

3. METHODS OF INVESTIGATION

3.1 HYDRUS-1D code – theoretical remarks

The computer program HYDRUS-1D numerically resolves using the method of final elements the advection-dispersion equation on the basis of the solution of the partial differential equation of Richards, which describes the water flow in a variably saturated porous medium (Šimůnek et al., 2008).

Resolving this equation requires the knowledge of two nonlinear functions, namely the soil water retention function and the hydraulic conductivity function. The hydraulic parameters describing the retention function and the hydraulic conductivity function were determined for each individual layer of the P-14 monitoring site (Figure 2) on the base of pedotransfer function analyses (Schaap and Leij, 1998; Schaap et al., 1998) using the ROSETTA program (Schaap et al., 2001) incorporated in the HYDRUS-1D. The procedure is described in details in Antonov et al. (2015).

3.2 Modelling schematization

A vertical profile model is elaborated for P-14 monitoring site. One-dimensional model is proposed and been suitable because of the observed downward water percolation of the alluvial deposits (Rahaman, 2016), although the code allows estimating the amount of the surface run-off as well. The schematization is in accordance with the field observation data using the information on the sediment layers' depth (Figure 3) with the respective five hydraulic parameters for each layer. The initial condition is arbitrary set to pressure head energy equilibrium with the groundwater level at –200 cm (the bottom of the profile). Thus, the bottom boundary condition is set to constant pressure head boundary equal to zero value (full saturation) and the upper boundary condition represents the number of time-variable boundary records, i.e. the precipitation records for April and July (Table 1).

For determination of the potential evapotranspiration ETp over the investigated area the Hargreaves Formula (Hargreaves, 1994) integrated in HYDRUS-1D (Šimůnek et al., 2008) was used for each of the ten-day periods of April and July, given by:

$$ET_p = 0.0023 R_a \left(T_m + 17.8\right)\sqrt{TR} \tag{6}$$

where R_a is extraterrestrial radiation in the same units as ET_p [e.g., mm d^{-1} or J $m^{-2}s^{-1}$], T_m is the daily mean air temperature, computed as an average of the maximum and minimum air temperatures [°C], TR is the temperature range between the mean daily maximum and minimum air temperatures [°C]. Extraterrestrial radiation, R_a [J $m^{-2}s^{-1}$], can be calculated as follows

$$R_a = \frac{G_{sc}}{\pi} d_r \left(\omega_s \sin\varphi \sin\delta + \cos\varphi \cos\delta \sin\omega_s\right) \tag{7}$$

where G_{sc} is the solar constant [J $m^{-2}s^{-1}$] (1360 W m^{-2}), φ is the site latitude [rad], ω_s is the sunset hour angle [rad], d_r is the relative distance between Earth and Sun [-], and δ is the solar declination [rad]. The last three variables are calculated as follows:

$$\omega_s = \arccos\left(-\tan\varphi \tan\delta\right) \tag{8}$$

$$d_r = 1 + 0.033\cos\left(\frac{2\pi}{365} J\right) \tag{9}$$

$$\delta = 0.409\sin\left(\frac{2\pi}{365} J - 1.39\right) \tag{10}$$

where J is the number of the day in the year [-].

4. RESULTS AND DISCUSSION

For the April`s simulation period with total amount of rainfalls of 48 litres per sq. m, only the upper 50 cm of the soil profile are subject to saturation (Figure 4). There is also some small increase of the moisture content between 50 and 70 cm. The rest of the profile stays unsaturated. In addition, the upper 50 cm of the profile are close to saturation after two consecutive days – 15th and 16th with heavy rainfall.

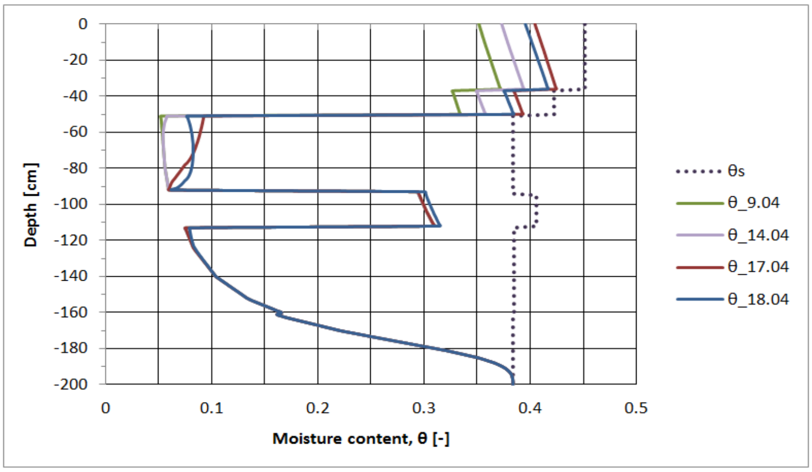

Figure 4. Selected moisture profiles through P-14 for the period of 9th to 18th April, 1965.

For the July simulation period with total amount of rainfalls of 15 litres per sq. m, only the zone between the upper two layers is close to saturation: 37%–38% moisture content of 42% content at full saturation (Figure 5). The rest of the profile is unsaturated throughout the whole period of simulation.

In addition, the relatively high value of the moisture content on the 1st of July is due to the initial condition of the elaborated model as the initial water content was set in energy equilibrium with the groundwater table at 200 cm depth.

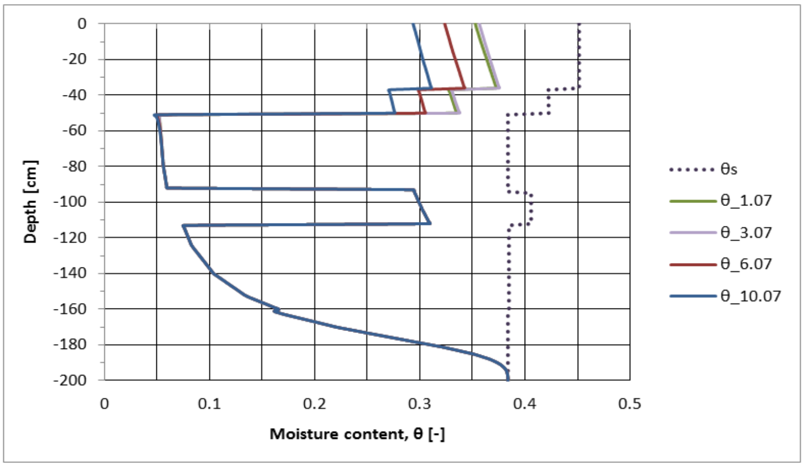

Figure 5. Selected moisture profiles through P-14 for the period of 1st to 10th July, 1965.

The main reason for the observed pattern of the moisture content variations is the evapotranspiration phenomenon, whose impact can be clearly seen with the dynamics of the actual surface flux graphs for each of the investigated periods (Figure 6 and Figure 7). When the value of the actual surface flux is negative it means that the infiltration rate prevails the evaporation one and vice versa.

In April, the main tendency of the flux is downwards, i.e. there is infiltration flux into the profile, reaching value of one cm per day on the 105th day (15th of April) equal to 10 litres per sq. m per day (Figure 6). There are two exceptions – between the 100th (10th of April) and 101st day (11th of April), and on the last day of the simulated period (18th of April), due to the combination of lack of rainfall and increased spring temperatures.

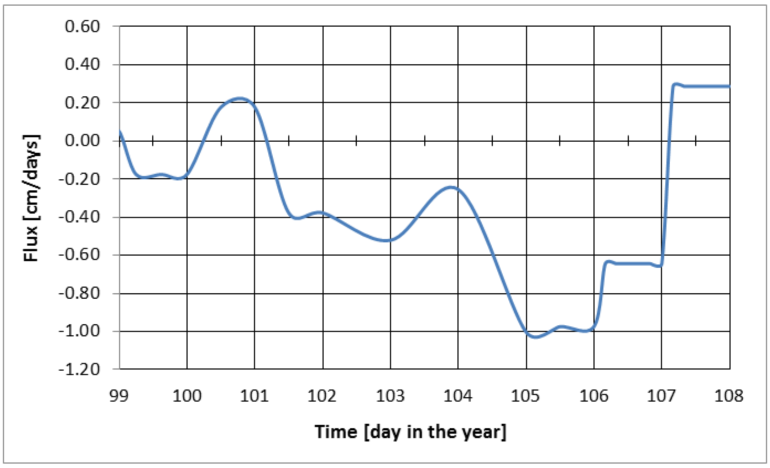

Figure 6. Actual surface flux coming into the P-14 profile in the period 09-18 April, 1965**.**

In July, the evapotranspiration phenomenon prevails the infiltration therefore the positive actual surface flux occurs most of the time (Figure 7). There is one exception on the

185th day (3th of July) when there is rainfall of 12 litres per sq. m leading to infiltration flux of 0.7 cm per day, the latter equals to 7 litres per sq. m per day. Hence, there should not be expected moisture conditions leading to saturation of the profile except if rain with a heavy intensity occurs.

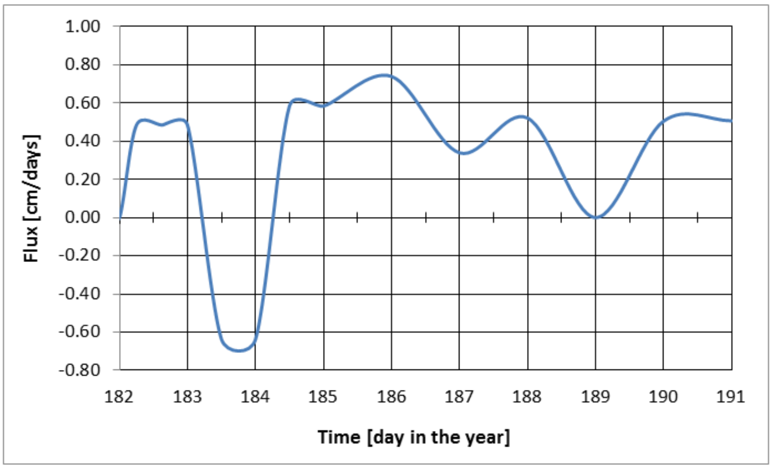

Figure 7. Actual surface flux coming into the P-14 profile in the period 01-10 July, 1965.

In addition, the code allows estimating the surface run-off which could appear after the rainfall event. The information is of importance because due to the terrain and geomorphological forms especially existence of negative ones an amount of water could be retained on the surface after the rainfalls and could lead to additional moistness. For April, this possibility is obvious (Figure 8). For the 103th day (13th of April) the amount of the surface run-off is 0.00045 cm per day, which is 4.5 litres per sq. m, and the amount of the fluxes for the day 105th and day 107th is similar.

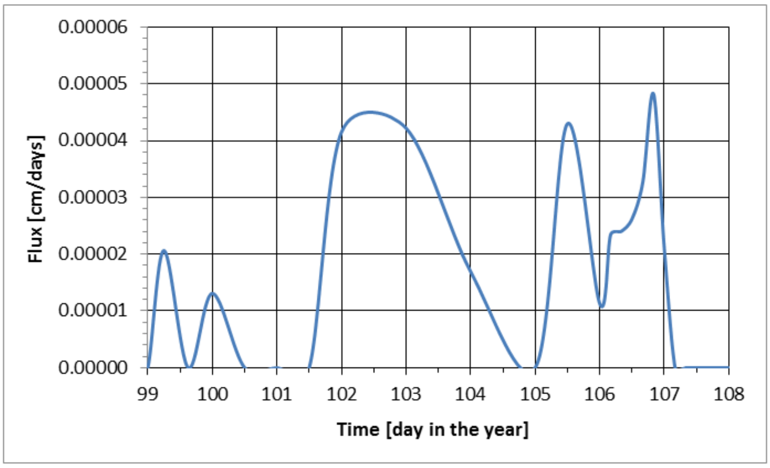

Figure 8. The amount of the surface run-off flux of P-14 site in April period.

As it could be expected due to the high temperatures and absence of rainfalls (with one exception) during the studies period of July, the amount of the surface run-off is almost negligible (Figure 9).

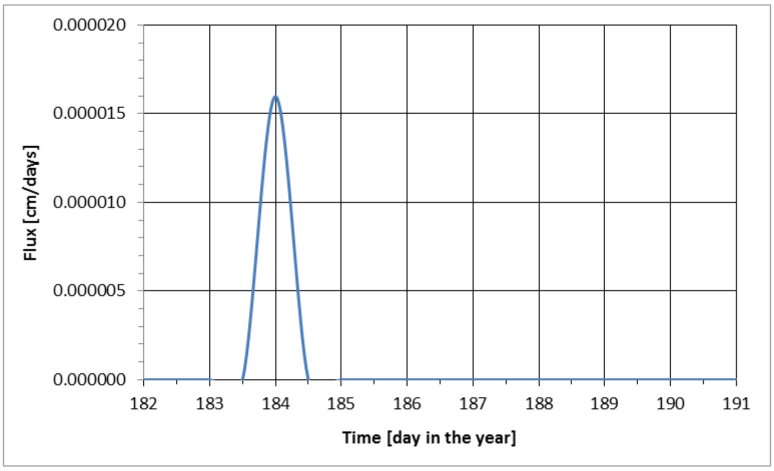

Figure 9. The amount of the surface run-off flux of P-14 site in July period.

As it was observed from the simulations, especially those in April, the layers close or equal to saturation were the upper two – between 0 and 36 cm, and between 37 and 50 cm below the surface; as well as the fourth one – between 93 and 112 cm depth (Figures 3, 4 and 5). Thus, it is important to understand the duration of saturation or sub-saturation period in order to estimate the possibility of redox potential changes. For that reason, the variable water content in the investigated periods is presented as a percentage from the maximum (at saturation) water content (θ_s). The latter is obtained from the pedotransfer function analyses (see Chapter 3). That was done both for April and July periods at three depths - at 18 cm, at 44 cm, and at 103 cm below the surface being the centre of the three investigated layers (Figures 10 and 11).

In April, the last four days (14th to 18th of April) due to the rainfall, the moisture content increases from 85% to 93% and then decreases to 90% from the maximum one.

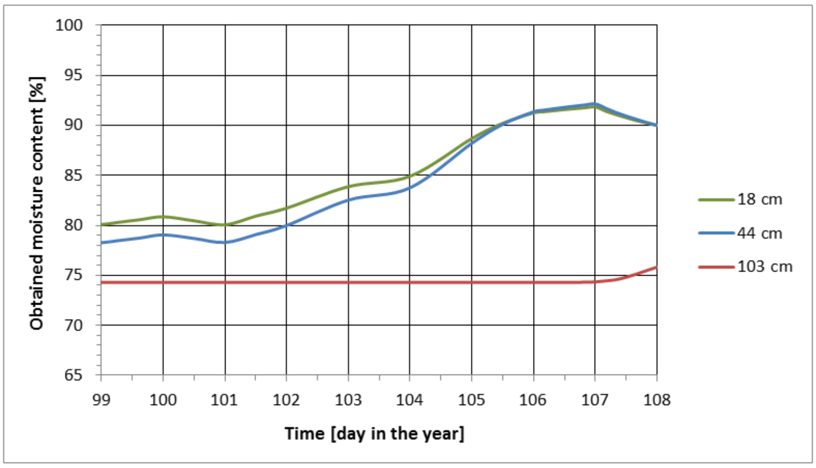

Figure 10. The obtained moisture content in percentage of the maximum water content, θs at three depths in the April period.

In the second period of simulations after the rainfall on 3rd of July, the uppermost layer reached 83% of the maximum water content, and the layer below – 80%. After this peak the moisture is constantly decreasing (Figure 11). Furthermore, the simulation results show that the fourth layer keeps a constant water content of 30%–31%, which is almost 75% of the maximum moisture value even in the period of high temperatures and intensive evapotranspiration. This observation is in connection with the fact that the layer is not subject to the direct influence of the evapotranspiration phenomenon. In addition, though the

Hargreaves Formula is being considered as proving some overestimation of the ET_p results (Alexandris et al., 2008), it is applicable for the present case study as it provides a kind of conservative values to the simulated results.

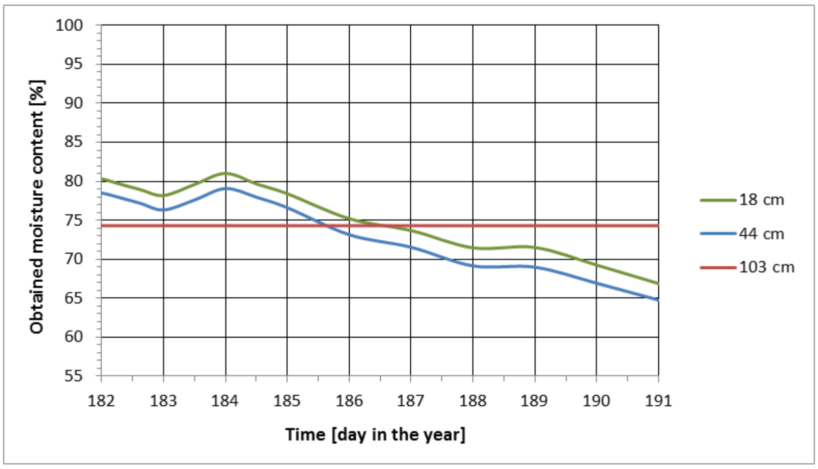

Figure 11. The obtained moisture content in percentage of the maximum water content (θs) at three depths in July period.

The received results from the simulations can be related to laboratory and field investigations of arsenic release in respect to redox changes under increasing water content conditions. Ehlert et al. (2016) performed a series of column tests with soil material from the Ogosta River floodplain simulating soil inundation. The results showed that after the first day of flooding, the redox potential began to decrease starting from Eh 300-400 mV, which level is typical for an oxic environment. Simultaneously, the arsenic concentration begun to increase in the solution. After 10 days of flooding the redox potential dropped to Eh 0-40 mV and As reached its maximum under anoxic conditions. Similar tendencies were reported by Xu et al. (2017) for paddy field soils. Before flooding, the Eh was in the range of 200 to 600 mV accompanied by very slow As release in the pore water. After the soil became water saturated, the redox potential rapidly decreased followed by intensive reductive release of As in the 10th day of the experiment.

Similar conditions with high moisture content in soil were observed only for two-three days during the April`s simulation with HYDRUS-1D (Figure 9), supposing that 90% of the maximum water content is very close to real saturation due to the closed pores. Considering the dynamics of the reductive release of As from the flooded soils as reported in the surveys cited above, water saturation for a couple of days is not long enough for significant arsenic mobilisation in the contaminated soil. However, in case of long-time rain falling for 6-7 days, which is not unusual for the spring and autumn seasons, a decrease of the redox potential can be expected followed by As release into the soil pore water.

5. CONCLUSION

The migration and faith of arsenic from pre-existing enriched spots situated in alluvial floodplain is subject to various processes and factors. One of them is the change of initially oxidizing to anoxic conditions hence leading to reductive release of iron and arsenic in the floodplain soil. The change of the redox state can be easily induced by the change of the soil moisture content due to flooding or heavy rainfalls.

In order to understand the effect of rainfall events over the occurrence and duration of saturation state of alluvium, a complex investigation was performed in a historically contaminated monitoring site in the Ogosta Valley. A vertical infiltration model coinciding with the vadose zone of the investigated spot was elaborated implementing the hydraulic characteristics of all impacted layers, which had been determined in previous studies. The meteorological scenarios included data from two ten-day periods in 1965 – April and July.

The simulation results show in general that saturation of the profile can be expected in case of rainfalls with precipitation values of 10 to 15 mm per day. Depending of the duration of the rainfall event, a state of saturation can be expected for particular layers or even for the whole profile. If the soil structure is predominantly sandy and the rainfall is in couple of days, the period of saturation is commensurable with the period of precipitation.

It was shown that the upper layers are subject to saturation for three of more days during the April meteorological scenario, and the water logging is additionally supported by the surface run-off amounts. The duration of the saturation state can last for longer periods, especially during the spring rainy maximum. For hot and dry months like July this possibility is quite low although some pre-surface layers (at about 40 cm depth) are also quite close to saturation after one day of rain. In this case of meteorological scenario, the duration of saturation state should be quite short.

Taking into account the results of studies of the kinetics of the reductive release of arsenic in flooded soils, the impact of two or three days' rainfall events cannot lead to significant arsenic release in the soil pore water or groundwater.

Finally, the proposed model enables understanding the moisture regime variations in the floodplain of Ogosta River and the simulations can contribute to the estimation of the arsenic mobilization conditions in polluted areas. As a further step, the results of the simulations can be coupled with data on arsenic dynamics in the soil pore water for more precise estimations of the impact of rainfalls to arsenic mobilization and transport in the contaminated floodplain soils.

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