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EFFECTS OF WASTE THERMAL WATER SEEPAGE ON THE SOIL-GROUNDWATER SYSTEM, WITH SPECIAL REGARD TO SUBPROCESSES OF SALINIZATION/SODIFICATION

Theses of Dissertation

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1. Introduction and research objectives

On more than two third of the area in Hungary, thermal water exploitation is intensified due to the advantageous geothermal facilities. Major part of the exploited thermal water has not reinjected into subsurface reservoires after utilization. Thus, it is disposed to surface waters through uninsulated ground channels in enormous volume. Sewage thermal water with a high concentration of salts, organic and inorganic contaminants infiltrates into the soil medium, affecting on soil and groundwater, as well as plants grown nearby. Hence, it is very important to identify alterations caused by waste thermal water seepage and its impact area.

To determine the characteristic contaminants of thermal waters utilized on the Great Hungarian Plain, a synthetic study has been presented based on environmental reports (Szmektit Bt., 2003-2008) on soils, groundwater and thermal water of 25 establishments utilizing thermal water. The thermal water seepage effect on soil-groundwater system was characterized with comprehensive evaluation of these reports. Two of these establishments (Cserkeszőlő-Spa/balneotherapy, Tiszakécske-Kerekdomb-horticultural estate/energetic purpose) were selected for detailed dissection. Three different soil types were identified on the sample sites (Chernozem, Phaeozem and Arenosol) according to the international, diagnostic soil classification system: WRB, 2006. Therefore, the pedology effects of thermal water seepage could be investigated on diverse soil types.

The goal was to evaluate waste thermal water seeping in ground channel, from the viewpoint of soil sodification/salinization/alkalinization using different indices (pH, total salt content, composition of ions, Mg %, Na %, SAR, soda content). The alterations in the physical-chemical parameters of groundwater and the modifications of the groundwater level and flow due to seepage were also researched. Adsorption of Na^+ (inducing sodification) in different soil types along the channel was followed by laboratory model experiments. Used thermal water infiltrating into the soil from the channel transports Na^+ vertically through unsaturated zone between the groundwater and the bottom of the channel. A predictive Na^+-transport model for 10-year period was created to assess Na^+-load contributing to Na^+-concentration of groundwater. Furthermore, the revealed alterations were confirmed by geostatistical analysis and the spatial delineation of the affecting processes was determined.

2. Materials and Methods

2.1. Sample area

Cserkeszőlő is located in the Tiszazug region of the Great Hungarian Plain. This study area with variable soil types (Chernozem, Phaeozem) is ideal for studying the effects of the used thermal water seepage since the spa has been supplying the channel continuously with waste thermal water for the past 50 years. There is no significant inflow to the channel owing to low relative relief.

The investigated horticultural estate in Tiszakécske-Kerekdomb with predominantly Arenosol is situated in the Pilis-Alpár sand ridge. The unlined ground channel has been loading with sewage thermal water periodically for the last 10 years, exclusively in winter.

Beside the thermal water effects on soil and groundwater, impacts on soil productivity were also observed since the adjacent areas of both channels are cultivated.

2.2. Sample method

The utilized thermal water, groundwater and soil samples were taken (Cserkeszőlő, 2008 fall; Tiszakécske-Kerekdomb, 2009 summer) at different sections and distances from the channel. Soil samples were collected every 20 cm to the groundwater table.

2.3. Laboratory methods

Chemical parameters indicating salinity/sodicity/alkalnity and physical parameters influencing pollution transport were measured. The pH was recorded in potentiometric way using a digital pH measuring device of Radelkis type. Total salt content was determined via electric conductivity. Carbonate content of soil samples was determined with Scheibler type calcimetry. The humus content was measured by spectrophotomerty, after H_2SO_4 digestion in the presence of $K_2Cr_2O_7$. Cation composition was determined using both 1:20 soil:ammonium-lactate extract via Atomic Absorption and Flame Emission Spectrophotometry and 1:5 soil:distilled water extract via Inductively Coupled Plasma Atomic Emission Spectroscopy. Based on these results, sodification parameters expressing the ratio of cations (Na_S% and SAR value) were calculated. Anion composition (from 1:5 soil:distilled water extract) and soda content was measured by titration. Soil texture was determined by the yarn test of Arany (the higher proportion of clayey particles, the higher Arany texture values). In the case of the soil samples having high humus content and/or Na^+ concentration, grain size distribution curve based on pipette method was illustrated in order to corrigate the results of the yarn tests. Porosity measurement was carried out via permeameter, with falling head method. Bulk density was determined gravimetrically.

The adsorption characteristic of Na^+ and the Na^+ adsorption capacity of soils can be described with adsorption isotherms, which represent the relation between the adsorbed quantity and the equilibrium solution concentration of the test component at a determined temperature. The amount of adsorbed Na^+ has important role in the aspect of physical soil degradation and sodification. During Na^+-adsorption model experiment, 5 grams of soil (m) were treated with 100 ml (V) of NaCl-solution of 200, 400, 500, 600, 800, 1000 mg/l (c0). These suspensions were homogenized for 3 hours by shaking till the adsorption equilibrium between the soil and the experimental solution come into existence. Subsequently, separation of the phases was performed by filtration. The concentration of the resulted filtrate is the equilibrium solute concentration (c_e). In view of these data, amount of adsorbed Na^+ per unit soil mass were calculated (q) based on the formula (1).

$$q = (V / m) * (c_0 - c_e) \qquad (1)$$

In order to devise adsorption isotherms, Na^+ concentration (c_e) of the measured equilibrium solution is represented depending on the calculated Na^+ amount adsorbed to unit soil mass (q). Modified Langmuir isotherm was fitted on the allocated points based on equation (2) by Microcal Origin 6.0.

$$Q = \left[\frac{a * k * c_e}{1 + k * c_e} \right] - e \qquad (2)$$

The "a","k","c_e","e" in the equation sign saturation concentration of the solid phase surface, the adsorption equilibrium constant, the equilibrium concentration in the liquid phase and the originally adsorbed Na^+ concentration at the solid phase surface, respectively. Adsorption parameters of the different soil horizons can be calculated from the equation of adsorption isotherm with extrapolation of the edited section. The differentia equation (3) indicates the values of soil horizons' Na^+-buffer capacity (partition coefficient) counted as first derivate of the edited sorption isotherm.

$$B = \frac{\partial q}{\partial x} = \frac{\partial}{\partial x} \left[\frac{a * k * x}{1 + k * x} \right] = \frac{a * k}{(1 + k * x)^2} \Big|_{x = c_e} \qquad (3)$$

The "B" variable signifies the partition of a given Na^+ concentration between the soil adsorption surface and the soil solution. The model experiment series was carried out with three replications, at 23 °C.

2.4. Modelling

The groundwater flow models of the plots were processed by Surfer 8, applying kriging method on the basis of the height of soil surface and the standing water table depths. In the unsaturated zone of the soil profile under the channel, Na^+ transport by infiltrating water was compiled with WHI UnSat Suite Plus 2.2, applying VS2DT module. The simulations refer to a 10-year interval according to 3 scenarios ("best case", "worst case" and "real case"). The boundary conditions of the scenarios were set in accordance with the laboratory results of soil and water samples, from the viewpoint of groundwater Na^+-loading risk.

1. "Best Case" Scenario: describes the condition when the Na^+ contamination of groundwater is expected to be minimal. Constant water of low-Na^+ concentration can be observed at low-level in the channel. Both groundwater level and Na^+-content is low during the year. There is Na^+-adsorption in the soil in this scenario. The real situation is underestimated in this case.
2. "Worst Case" Scenario: the most pessimistic estimation, the most dangerous situation of groundwater Na^+-contamination is assumed. The highest measured concentrations of Na^+ appear in the channel as an input over the year, with the maximum water level in the channel. There is no Na^+-adsorption in the soil, thus the Na^+-load of groundwater reaches the maximum. The highest measured groundwater table and the highest groundwater Na^+ concentration were fed. In this scenario, real situation is overestimated.
3. "Real Case" Scenario: This model setting approximates the (real) actual Na^+-transport conditions the most. It was made applying the field observations and laboratory test results of the samples from the study area. The adsorption capacity of the soil is also taken into account.

2.5. Geostatistics

Summarizing the effects of used thermal water in the Great Hungarian Plain, the calculated minimum, maximum, mean and standard deviation values of thermal and surface water, groundwater and soil data were compared with the operative limit values. In the case of thermal water, the results were evaluated according to the regulation of the Ministry of Environment and Water No. 28/2004 (XII. 25), the collective decree of the Ministry of Environment - Ministry of Agriculture and Regional Development No. 9/2002 (III. 22) and its amendment No. 219/2004 (VII. 21). The soil and groundwater limit values are demonstrated in the joint ordinance of the Ministry of Environment and Ministry of Public Health No. 6/2009 (IV. 14). Based on these, both the elements exceeding the limit values and the frequency of contamination were determined. A given component is considered to be typical contaminant if more than 50 % of the cases exceed its limit value.

In the case of Phaeozem and Chernozem from Cserkeszőlő, geostatistical analysis is presented in order to validate the effects of used, seeping thermal water on soil parameters. In the course of statistical analysis, SPSS 12.0 for Windows software assuring correlation analysis, principal component analysis and discriminant analysis was applied in order to identify perceived processes and isolate spatially the channel-effected and not-affected (control) groups of soil samples.

3. Results

3.1. Characteristic contaminants in used thermal water of the Great Hungarian Plain and their effects on the soil-groundwater system

In the waste thermal water from the studied region of the Great Hungarian Plain, the specific contaminants are ammonium, As, Hg and Pb. Furthermore, Na^+ predominance also can be observed among cations. In seeping surface water of thermal water origin, high Na % and ammonium of high concentration are considered to be environmentally risky. Hg concentration exceeds limit values in the surrounding groundwater as much frequently as in general. In addition, limit value exceeding concentrations of the risky metallic elements in thermal water and surface water was also detected in ground water, although their frequency is less than 50 %. The high-Na ratio is also evident, despite the fact that none of laws defines limit. The noticed similarity in the contaminants of thermal water and groundwater suggests thermal water effect on groundwater. In the soil, total salt content and Mg_S% transcended limit concentration of salinity/sodicity. Exclusively pH value exceeded the limit value in most cases. In some cases, concentration of microelements (Hg, As, Ni), can be observed as contaminants also in thermal water, was higher that ones in the operative limit. Among contaminants in the soil, total salt content, Mg_S% and pH appeared in high frequency, which variables related to salinity/sodicity/alkalinity sub-processes. Besides, salt accumulation, physical degradation and alkalinity can be assumed.

As for the effects on groundwater and soil by the infiltrating thermal waters used in the investigated region, it can be assessed that exclusively Na^+ and ammonium of groundwater contaminants originate from thermal water. Seeping thermal water exerts influence on the soil by plus salt transport/supply resulting in salt accumulation. Despite the fact that the thermal water salinity has not exceeded the limit value, total salt content in most cases is more than 500-1000 mg/l prescribed by the norm of irrigation water quality (Darab & Ferencz (1969)).

3.2. Chemical properties of the waste thermal water in two selected sample area and their effects on the groundwater

In the case of two out of 25 investigation area (Cserkeszőlő, Tiszakécske-Kerekdomb), more detailed investigations were carried out to gain information about the potential impacts of used thermal water seepage.

It can be established that the high Na^+-ratio in the waste thermal water is characteristic in both study areas (just as the previously described investigated region of the Great Hungarian Plain). Therefore, they can be classified into irrigation water quality class IV, which is unsuitable for irrigation. Used thermal water in Cserkeszőlő and one in Tiszakécske-Keredomb belongs to the Na-Mg-HCO_3 and the Na-HCO_3-Cl chemical type, respectively, which supports Na-dominance. As a result of the above mentioned, their sodification impact is confirmed.

In the case of soils having sandy texture along the channels, Na^+ in thermal water with high Na % can get into the groundwater in higher amount. Being high saturated hydraulic conductivity and low clay content, Na^+ can not be adsorbed in high quantity but is able to get into the groundwater. Consequently, the appreciation of Na-dominance in the groundwater can be detected over change in the groundwater chemical type, direct increase in Na % and deterioration in irrigation water quality through more categories. Increase in Na^+-concentration of groundwater is not typical of the soils with higher clay content since these are capable of adsorbing more Na^+. If increment in Na % can be observed in the groundwater near the canal then it occurs in an indirect way as a consequence of decrease in Ca^{2+} and Mg^{2+} concentration.

The alkalinity effect is caused by salts of alkali hydrolysis (Na_2CO_3, $NaHCO_3$) in thermal water getting into the groundwater. The highest degree of alkalinization was also detected in the groundwater of profiles with sandy texture.

The natural flow of groundwater is blocked and more or less modified by the channels. This modification rate depends on the angle formed by the direction of initial groundwater flow and the position of the channel. The changes in the physical-chemical parameters of groundwater around the channels are induced by the leakage of waste thermal water having different chemical characteristic from groundwater, together with the modified groundwater flow. These effects may appear differently in the other sections of the channels. For example, on the left bank of the upper channel section (Cserkeszőlő), total salt content of groundwater is locally decreased by outflowing used thermal water near the channel, reducing the rate of salt accumulation processes. In contrast, on the right bank of the lower section, the outflowing water takes a damming effect on the groundwater having originally high salt content. Thus, compared to the upper section, total salinity is increasing near the channel promoting the development of accumulation/salinization processes of soils.

In the case of channels continuously supplied with waste thermal water (e.g. ones related to spas) increase in the level of the groundwater table as permanent impact can be described. In Cserkeszőlő, salt accumulation is expected due to the groundwater level rise above the "critical groundwater table". In the case of channels periodically supplied with waste thermal water (e.g. ones related to horticultural estates) considerable fluctuation in the groundwater table can be observed comparing the winter with summer period. It has not approached the „critical groundwater table" (e.g. Tiszakécske-Keredomb) making the development of salt accumulation less likely.

Physical effects include even the thermic effect, which led to higher temperatures increase in the groundwater owing to balneologically used seeping water, than that of energetic utilization.

Based on the aforementioned, physical-chemical changes in the groundwater induced by seeping thermal water reflect artificial anthropogenic effect. In soil, getting contact with the poor quality thermal- and groundwater, sub-processes of salinization/sodification can be expected.

3.3. Effect of used thermal water on different types of soils

3.3.1. Characterization of the thermal water seepage effects based on the WRB (World Reference Base for soil Resources, 2006)

Soil types of the plots were classified into reference groups of the WRB (2006) in order to determine if degree of the soil alterations caused by seeping thermal water justifies application of the given prefix or suffix qualifiers and classification of the profiles into different soil groups. Prior to the classification, natural (natric, salic) and/or anthropogenic (hydragric, irragric) diagnostic horizons reflecting sodification/salinization and effects of the thermal water seepage were defined.

It can be concluded that the natric and salic horizons were not presented in the profiles hence the salinization and sodificanion forming them were in initial phase. Hydragric and irragric horizons, indicating increased water effect due to human impact, were perceived neither contrary to our preliminary expectations for the appropriate thickness of the horizon or textural requirements were not met the criteria.

The soil profiles close to the channel were classified into Orthicalcic Luvic Chernozem (Pachic) and Calcic Luvic Phaeozem (Abruptic), whereas denomination of the control ones was expanded with the suffix Anthric reflecting differences owing to cultivation. Beyond later suffix, other ones could not be applied since there was no so significant modification in diagnostic properties that can support the different classification of the soils far from channel. In the soils of Tiszakécske-Keredomb, diagnostic variance can be observed only on the lower section of the channel. The control profile meets the criteria of the typical Arenosol (Haplic Arenosol); the soil near the channel (Albic Arenosol), in turn, has a light-colored subsurface leaching horizon, which can be characterized with coarser texture and lack of structure.

In Cserkeszőlő, although there is just 285 m between the sample points downward the canal yet profiles can be assigned into different soil groups (Chernozem-Phaeozem) over increased leaching on the lower section. This all reflects soil development formed by the water seeping from the channel.

3.3.2. Evaluation of the salinity/sodicity/alkalinity effects of waste thermal water seepage on soil by different indicators

Assessment of potential salinization/sodification/alkalinization due to used thermal water seepage was realized based on main parameters characterizing these processes. pH (H_2O); total salt content (together with the profiles of soda and lime content); soda content, Na_S %, SAR value were indicators of alkalinization; salinization and sodification, respectively. Due to agricultural production around the canals, it was important to evaluate the agronomic aspects.

In the studied Chernozem profiles in Cserkeszőlő, weak salt accumulation with Na-salt dominance can be detected both in the sample points close to and distant from the channel. The rate of salt accumulation is higher in the profile next to the channel than in the control one. Increment in the level of groundwater with high salt content above the "critical groundwater table" is attained by sewage thermal water outflowing from the canal. Thus, salt balance in the profile has become positive the accumulation has dominated. Higher salt maximum can be observed in the profile close to channel compared to the control one owing to salt input not only from the groundwater but from the channel. The value of salt maxima diminishes whereas the depth of that increases ever farther from the channel. The groundwater of the profile near the channel is closer to the surface than that of the distant one as a consequence of outflow as well as salt accumulation level is located closer to the surface than that of the control. Na^+-concentration of the profile next to the channel is increased by Na^+ content originated from seeping thermal water causing direct enhance in the Na_S% and the SAR value. The extent of the detected Na^+ accumulation, however, has not approached the soil degradation limit (12-15 Na_S%). The effects modifing soil have not manifested such an extent in the Chernozem yet that could deteriorate soil fertility on the channel adjacent areas.

In Phaeozem profiles, weak salt accumulation was detected, which exceeds the rate that of experienced in Chernozem profiles. The intensification of the salt accumulation has not unambiguously depends on the distance from the channel. On the channel adjacent areas, role of Na-salts has to be emphasized in salt accumulation. In the salt accumulation of the control point, in turn, Na- and Ca-salts together take part, which confirms rather groundwater origin. The soda from seeping thermal water appears in the groundwater and induces alkalinization in the subsoil of the profile near to the channel. Thus, alkalinization effect of the used thermal water can be detected indirectly through groundwater. Phaeozem profile has not adsorb large portion of the incoming Na^+, but let it leak into the groundwater resulting high Na % near to the channel. Disadvantageous changes in the Phaeozem profiles can not be established from agronomic viewpoint as both the alkalinity and salinity impact manifest itselves under the root zone.

In Arenosols with sandy texture, the infiltration is less inhibited and leaching is much emphasized than soils having higher clay content and more compact structure. Therefore, salt maximuma appear in the zone of groundwater fluctuation. All topsoils were characterized with low salinity. The salt maxima have not reached the salt accumulation limit concentration yet (0.05-0.1%). Na_S% and SAR values have not indicated sodification. In the profiles with high saturated hydraulic conductivity and low clay content (low buffer capacity), groundwater is affected by both the salts and Na^+ intensifying its salinization/sodification impact. This process is only local owing to the channel-parallel direction of groundwater flow. The alkalinity impact of the seepage is manifested indirectly through groundwater by increased soda and HCO_3^+ concentration surrounding the channels. Based on these observations, thermal water effects on Arenosols close to the channel are slight and only affect on the lower regions of the soil around the groundwater table, or depth between the infiltration and groundwater fluctuation zone. Therefore, in the adjacent areas, potential yield is considered to be 100 %.

In general, it can be stated that:

- Salt accumulation has evolved in the profiles with mechanical composition heavier than sandy loam that have the groundwater level beyond the "critical groundwater table" and the salinity of groundwater transcending 1000 mg/l.
- Higher degree of salt accumulation has manifested due to the higher total salt input and various textural types in the profile. The textural changes can contribute to the accumulation and concentration of the high salt content water within the profile leading to the precipitation of salts. Excess salt input is provided by the sewage thermal water outflowing from the channel for the nearby profiles compared to controls. Near the channel, higher salt maximum can be observed in shallower depth as a consequence of the increased groundwater table, plus salt content and the capillary lift maintained by evaporation/evapotranspiration. The level of

salt accumulation is determined by the root zone depth of the plants living or cultivated there.

- It can be claimed that not just thermal water effect can cause salt accumulation but it determines the extent and level of the accumulation.
- The most significant effect of thermal water seepage is regarded to increase in the level of groundwater with originally high salt content above the "critical groundwater table" promoting salt accumulation in the soil.
- On the upstream of the channel, groundwater level is always higher than that of the downstream section since the channel bed slopes from upper section to lower one determining the depth of the groundwater table. The salt accumulation levels are influenced by the groundwater level so salt accumulation is of less depth in the upper section than in the lower one.
- Na^+ effect of the infiltrating thermal water has to be emphasized. Owing to high mobility and small adsorption affinity (relative to the other exchangeable cations) of the studied ion, it currently does not cause sodification in the profiles but entering groundwater can spread with its flow. Notable Na^+ effect would be manifested by sodification in soils if this process was traced either in a longer period or in the lowest point of the groundwater flow system where the transported high concentrations of Na^+ could be accumulated taking the place of the more strongly associated ions on the adsorption surface.
- The alkalinity effect of used thermal water regulary appears in the subsoil indirectly through the groundwater. This effect is generated by the soda and HCO_3^- excess of thermal water origin.

3.3.3. Alterations in the characteristic ion composition of the soils depending on the distance from the channel

Apart from Phaeozem, increase in Na^+-concentration is reflected in each soil profile along the canal. Na^+ distribution in the profiles varies in different sections of the channels; ion maximuma can be detected in ever deeper horizons of the profiles downstream. Na^+ dominancy is also shown in the ion diagrams of the groundwater near the channel. Therefore, a portion of Na^+ is adsorbed but the Na^+ load of groundwater could not be eliminated by soils.

Excluding Chernozem profiles, each soil type has lower Mg^{2+} concentration near the channel than in the control point. Thus, in soils along the canal, the typical process is Mg^{2+} mobilization.

Among anions, HCO_3^- plays an important role in the Chernozem and Phaeozem profiles. Close to the channel, HCO_3^- concentration decrease appeared in the Chernozem, while realignment of the ion can be seen in the

Phaeozem. In the case of Chernozem and Phaeozem, SO_4^{2-} is rearranged along profile by the effect of the channel. Increment in SO_4^{2-} concentration also occurred in the Arenosol profile near the channel, which can be detected in the groundwater, as well.

The seeping thermal water causes redistribution of Cl^- in every profile and decrease in its concentration exclusively in the case of Phaeozem. In this section of the canal, Cl^--concentration of the seeping thermal water is very low so this easily mobilizing ion can be desorbed from the soil. There is no dominant among anions in Arenosols, their ratio can be considered to be balanced.

The level of the ion maximuma, the degree of concentration increment is determined by the saturated hydraulic conductivity (depending on the texture and structure of soil profiles); the soil type, ion composition of groundwater and thermal water, respectively.

3.3.4. Evaluation of the Na^+-adsortion in the different soil types

The adsorption of Na^+ concentration infiltrating from the canal into different types of soils can be followed by adsorption model experiment. After devising adsorption isotherms, adsorption parameters can be established. Since Na^+ adsorption is weak hence adsorption curve is close to linear (in 200-1000 mg/l Na^+ concentration range) making difficult to define the saturation state. Therefore, adsorption parameters, calculated by extrapolation of the isotherms (eg. maximum adsorption capacity, originally adsorbed Na^+-concentration), is suitable only for estimation due to errors.

It can be established that order of the greatest potential Na^+-adsorption capacity in the soils is as follows: Arenosol<Chernozem<Phaeozem.

The differences in the absorbable Na^+ amount between the soil horizons depends on the different humus, clay and carbonate content of each horizon (determining the size of the adsorption surface and the amount of the active sites), the original Na^+ saturation and the adsorption equilibrium constant. The latter two parameters can be calculated by using the modified Langmuir isotherms applied in the isotherm fitting.

The determined adsorption limit concentrations signify the equilibrium solution concentration above which adsorption, under which desorption can be observed in the profile. This concentration is practically equal to the equilibrium Na^+ concentration of soil solution and interfacing soil at the sampling moment. This parameter also can be appointed from the adsorption isotherms; accuracy of that is the same high as one of the isotherm fitting so has high precision (in most cases $0.7 < R^2$). The adsorption limit concentrations of Chernozem soil are 400 mg/l in the A-and C-horizons and 577 mg/l in the B-horizon. In the Phaeozem profile, adsorption limit concentration on examined concentration range can be given only refer to the B-horizon (800 mg/l). In the A-horizon it is less than the lowest Na^+-concentration used in the model experiment (200 mg / l); in the C-horizon it is greater than 1000 mg/l. In the Arenosol profile, adsorption limit concentration can be given as 290 mg/l, 196 mg/l and 295 mg/l in the A-, B- and C-horizon, respectively.

Adapting the results of the model experiment to natural conditions it can be given that adsorption or desorption occurs in the horizons, based on the characteristic adsorption limit concentration of soil horizons and the Na^+ concentrations of the infiltrating thermal water. Chernozem profile is affected by thermal water with 570 mg/l Na^+ concentration inducing adsorption in both A- and C-horizons and weak desorption in the B-horizon. Towards the lower section, Na^+-concentration of sewage water in the channel decreases to 430 mg/l causing adsorption in the A-horizon and desorption in both the B- and C-horizons of Phaeozem profile. The Arenosol profile is took effected by waste thermal water of 340 mg/l Na^+ concentration, which would result in different degree of adsorption in each horizon. Simplified situation (the worst situation) is reflected by the model experiment, hence among natural conditions, ions competing with Na^+ and adsorbing more strongly than Na^+ (e.g. Ca^{2+}) take part in the adsorption of the soil reducing the amount of adsorbable Na^+.

The adsorption capacity of soil is an important factor in the groundwater protection. In the case of Phaeozem, A-horizon is capable of adsorbing Na^+ in high amount on the experimental concentration range. This is not beneficial in terms of reducing the Na^+ load of groundwater. In contrast, Chernozem and Arenosol profiles adsorb Na^+ much more effectively in the C-horizon, which have a favorable effect in the reduce of groundwater Na^+ load.

The partition coefficient, i.e. the buffer capacity can be calculated as the first derivative of the rise of the isotherm curve. The split of the incoming Na^+ concentration between the soil and soil solution is indicated by the partition coefficient. In the experiment, Na^+ concentration of the initial solution increases while buffer capacity of the treated soil decreases. The limited adsorption surface is able to adsorb decreasing proportion of the incoming Na^+ content, thus increasing proportion of that remains in the solution and reaches the groundwater. The same decrease in the buffer capacity can be observed even in natural conditions, when as a result of continuous Na^+ supply, Na^+ is accumulated in the soil over the years, thus the incoming Na^+ concentration can be adsorbed in less amount. It can be found that the Phaeozem has the highest buffer capacity of the examined three soil types and Arenosol has the lowest.

Linear sections of the adsorption curves being different distances from the saturation maximum was revealed by the experiment. It was shown if 1000 mg/l Na^+ containing thermal water (chosen the maximum concentration in the experiment) was seeping on the plots instead of the current approx. 500 mg/l, it would not saturate the entire adsorption surface. The soils have free adsorption capacity of Na^+ deriving from thermal water seepage in the future. The proportion of the maximum adsorbable Na^+ concentration can be counted based on the measured isotherms in the case of about 500 mg/l effective concentration, and e.g. 1000 mg/l effective concentration. Consequently, if Na^+ concentration increment in seeping thermal water was supposed to be up to 1000 mg/l, the degree of saturation would be high and rapid in the A-horizon of the Chernozem (14.58% → 27.65%), and in the B-(1.17% → 6.56%) and C-horizon (4,17% → 11.94%) of the Arenosol. In other cases, the degree of saturation owing to an increase in effective concentration has not refered to the appearance of degradation processes. These calculations also show that in the case of Phaeozem, Na^+ mobilization, desorption would occur in the subsoil, therefore these soils would not be able to sufficiently reduce the Na^+ load of groundwater. In instance of Chernozem and Arenosol, Na^+ load of groundwater would be reduced by adsorption, but the profiles themselves would represent sodification.

3.3.5. Na^+ transport models of the unsaturated zone under the canal

Na^+ transport models of the unsaturated zone under the canal were carried out on two selected soil types (Phaeozem, Arenosol) of the investigation areas applying three hypothetical scenarios ("best case", "worst case", "real case"). Success of soil profiles in the inhibition of groundwater Na^+ load, based on the results of the models can be concluded based on the proper input data. The program is suitable for model temporal changes of groundwater Na^+ load and present it in selected time steps. The date of real Na^+ contamination reaching the groundwater can also be determined. Adsorption and desorption occuring in different depth of the profiles can also be inferred from the model.

On the basis of the "real case" models of unsaturated Na^+ transport, it can be sum up that in Phaeozem, Na^+ concentration in the groundwater is higher than in the seeping water. Phaeozem profile having higher clay content (clayey-loam texture) is saturated by the investigated ion rapidly, thus the model shows desorption after the third year.

In the case of Arenosol, Na^+ concentration of groundwater is lower than that of the seeping water. Therefore, the Na^+ load of groundwater strongly depends on the Na^+ adsorption ability of the profiles. The Na^+ concentration of infiltrating water is reduced by the 40 cm thick loam layer below the channel. In spite of adsorption in the loam layer, due to the textural change (loam→sand), desorption appears in the sandy layer increasing the Na^+ load of groundwater. Soil profile above the groundwater table is able to reduce Na^+ load in the first five years, however, groundwater is loaded with Na^+ in the tenth year according to the model. The fact that without adsorption (and loam layer), Na^+ load would reach the groundwater after the first year confirms the important role of adsorption. Thus, between the given boundary conditions, the extent of Na^+ contamination of the groundwater is slowed down by the loam layer of the Arenosol profile.

Compared to the Na^+ saturation of the Phaeozem profile, slower rate of saturation is expected in Arenosol between the given boundary conditions. Thus, the appearance of sodification can be required later in the Arenosol profile; however, Na^+ load through the groundwater may affect surrounding subsoil from the tenth year.

Decrease in Na^+ buffer capacity of the both modelled profiles could be pointed with the time passing. From the same Na^+ concentration input, soil is able to retain lower proportion. Therefore, Na^+ concentration of the infiltrating water is increasing. Continuous Na^+ input during ten years can saturate the absorption surface of the soil to a large degree that infiltrating water (as relatively diluted solution) gives rise to desorption, mobilizing Na^+ into the groundwater from the soil.

Diluting or loading impact of a mobile contaminant on groundwater is strongly dependent on the concentration ratio measured in the infiltrating thermal water and that of the groundwater. In addition, it depends also on the adsorption capacity and saturation state of soil connecting the channel, which can attend in the reduction of contaminant concentration entering groundwater.

The Na^+ transport is determined by the structural and textural conditions of the profile, influencing the pore structure properties and the saturazed hydraulic conductivity (ratio of gravitational water and capillary water), on the one hand and the rate of clay content having emphasized importance in Na^+ adsorption, on the other hand.

Original vertical Na^+ ditribution of the profiles shows increasing Na^+ content towards the groundwater table. Equalization of the vertical Na^+ distribution within the profile can be observed by processes evolving between the infiltrating thermal water and the soil, based on the model. Steady Na^+ gradient developes in the unsaturated soil zone in the tenth year, bridging the Na^+ concentrations of the seeping water and groundwater.

Based on the aforementioned, sodification is not manifested itself at the time of the sampling work, however, during a long-term deposition of high

Na % waste thermal water, infiltration and accumulation of Na^+ on the adsorption surface can support the Na^+ load of groundwater beside the sodification of the profiles near channel.

3.3.6. Identification of used thermal water seepage impacts by geostatistical analysis

Modifications in the investigated diagnostic soil parameters generated by the seepage of thermal waters, shown in the preceding chapters, were confirmed by geostatistical analysis. Principal component analysis for the 11 investigated diagnostic parameters was executed. Four independent principal components were generated representing 93.03 % of the total variance. Each one of these can be corresponded to an independent soil process, for example Mg^{2+} mobilization, salinisation. In the multivariate space of the principal components, discriminant analysis was applied. The positive and negative elements of the computed discriminant function (D=0,65*FK4-0,45*FK1-0,28*FK3+0,18*FK2) were separated forming the axes of the discriminant diagram. Finally, as a result of discriminant analysis, soil samples was succesfully classified (with 85,7 % propriety) into the correct a priori groups ("thermal water affected" or "control") according to the distance from the channel. The calculated discriminant function is appropriate to predict the group of any further soil sample from this investigation area. Later, the extent of the impact area of the channel can be monitored in this way.

The role of the identified processes in distinguishing of sample groups is indicated by the discriminant function. Mg^{2+} mobilization is the main process, and salinisation is the most insignificant. Salinization processes (compared to the control samples) are seems to be rudimentary along the canal.

Summarizing the results of geostatistical analysis:

- in the soil, ion exchange and adsorption processes of Na^+ are presented (Na^+ accumulation);
- ion mobilization and leaching effect (Mg^{2+}-mobilization, Ca^{2+} mobilization, carbonate leaching) can be detected as a consequence of increased outflowing of sewage water near the channel;
- simultaneous increment in humus and K^+-content can be established owing to the adequate water supply, higher temperature, increased plant and microbial activity and the decomposition of plants close to the channel
- weak soil salinization can be detected adjacent the canal, which is indicated by the salt accumulation and the increased soda content.

3.3.7. Spatial allocation of thermal water effects

The spatial extent of the aforementioned effects is determined by the physical parameters of soils (saturated hydraulic conductivity, mechanical composition, water capacity, etc.) and the direction of the groundwater flow (due to the transported Na^+ and salts). Since the original direction of the groundwater flow is modified by established channel, indirect role of canal situtation in the contamination transport can be stated. If the groundwater flow is parallel to the channel, impacts on groundwater are local around the canal, hence contaminants entering the groundwater are transported parallelly the channels. If the direction of canal and groundwater flow has any angle, the extent of the effect depends on the outflow or damming impact of the channels on groundwater.

It was found that the impacts of the channel on groundwater and soil are considered to be local (<30-35 m from the channel) on the Cserkeszőlő plot. An increasing trend is shown in the degree of salt accumulation and alkalinization in the profiles downsteam the canal.

On the Tiszakécske-Keredomb plot, alkalinization can also be detected in the control points, but the effect is decreasing ever farther from the channel. Increment in the total salt content can be observed exclusively in the upper section, near the canal. In profiles having sand-texture and low groundwater table, infiltration is dominated by gravitational water flow; therefore salts transported rather vertical down than lateral, resulting in local effects. The sandy profile with loam layer has a greater ability to adsorb Na^+. In spite of this fact, Na-effect of thermal water can still be detected in the groundwater, but remains local. Downstream the channel, the range of the effects is decreasing and appearing in ever deeper horizons.

Thermic effect of thermal water on the groundwater can be established on the areas around the channels. Past the channel, temperature is rising by more °C in groundwater compared to the control in each case. If the temperature is compared to the average soil temperature (14 °C), the effect can be noticed even in the control points. Decline in the thermic effect is pointed downstream the channel since temperature of flowing thermal water is progressively diminishing due to heat release to the environment. Beyond temperature and quantity of the deposited sewage water, heat effect on grounwater is defined by the typical heat conducting/insulating property of the adjacent soils, as well as the groundwater table depth under the canal.

Publications

Balog, K., Farsang, A., Puskás, I. 2011. Characterization of the soil degradation impact of waste thermal waters on the Southern Great Hungarian Plain (Case study about the risk of sewage thermal water seepage on soil medium), Carpathian Journal of Earth and Environmental Sciences, 6/1, 229 – 240., IF: 0,606

Balog, K., Farsang, A., Czinkota, I. 2011. A használt hévíz szikkadásának talaj-degradációban betöltött szerepe, Hidrológiai Közlöny, 91/2, 55-60.

Balog, K., Farsang, A., Czinkota, I. 2011. Használt hévíz szikkadás hatására bekövetkező degradáció a talaj-talajvíz rendszerben alföldi mintaterületen, Talajvédelem különszám, in press

Balog, K., Farsang, A. 2010. The role of waste thermal water in the soil degradation, EGU Conference 2010., Vienna, Geophysical Research Abstracts 12., EGU2010-4059, 2010, EGU General Assembly 2010 © Author(s)

Balog, K. 2009. A használt termálvíz-szikkasztás talajtani és környezeti hatásai, In: Kiss, T. (szerk.) Természetföldrajzi folyamatok és formák, Geográfus Doktoranduszok IX. Országos Konferenciájának Természetföldrajzos Tanulmányai, 263-276.

Balog, K., Farsang, A. 2009. Használt termálvíz szikkasztás hatásainak vizsgálata különböző talajtípusokon (Esettanulmány cserkeszõlõi mintaterületen) In: Galbács, Z. (szerk.) The XVI. Symposium on Analytical and Environmental Problems kiadványa, 300-304.

Balog, K., Farsang, A. 2009. Secondary salinization caused by used thermal water seeping, IUSS Salinization Conference, Budapest, Program and Presentations, 4.

Balog, K.., Farsang, A. 2008. Thermal Water Exploitation and It’s Environmental Risk in Hungary, Eurosoil Conference 2008, Vienna Poster, Book of Abstracts, 581.