**Final Scientific Report**

# Arsenic contamination of Ogosta river: Linking biogeochemical processes in floodplain soils with river system dynamics (ASCOR)

## 1. Introduction

The sustainable management of land, which has been heavily contaminated by industrial or mining activities, poses an important challenge to many industrialized countries, including Bulgaria. This project focused on arsenic (As) contamination in NW Bulgaria, where the floodplains of the Ogosta river received large amounts of As-rich mining wastes near Chiprovtsi between 1964 and 1979. The research project had three main goals, which were addressed in three work packages (WP1–3):

- WP1 – Investigation of the magnitude and spatial distribution of As contamination in the floodplains of Ogosta river (Bulgaria) using an integrated approach based on topography, hydrology, and geochemistry (WP1, lead partner: BAS).
- WP2 - Improvement of our process-understanding of As speciation and mobility in highly-contaminated, mining affected river floodplains during alternating periods of high/low flow and flooding/drainage, respectively (WP2, lead partner: ETH).
- WP3 – Exploration of novel approaches for integrating process-oriented, molecular-scale knowledge (WP2) and river-system scale information (WP1) to better understand As dynamics, As fluxes, and impacts on water quality at the river-system scale (lead partners: ETH and BAS).

This final report briefly summarizes the activities and results achieved in the three work packages. It is structured according to the tasks outlined in the original proposal.

## 2. Summary of research results

### 2.1. Results of WP1

### Task 1-1. Building a GIS database for the upper Ogosta river catchment

During the life time of the project data on soil, topography, groundwater, hydrological and hydrogeological settings has been generated and organized in Excel files and in data layers to be used and processed in GIS environment. Detailed orthophoto mosaics and digital terrain and surface models of the Ogosta Valley have been generated from airborne laser scanning (ALS). Series of maps of morphographic indices and a map of geomorphographic units of the Ogosta floodplain, flood maps of historic events and of inundation induced by rainfalls with return periods 2, 5, 20 and 100 years, a map of the groundwater table depth, and a map of groundwater vulnerability to As contamination in the Ogosta Valley have been produced. New information on floodplain soil and sediment structure, soil texture and pH, concentration of As and heavy metals in river water, groundwater and in certain soil depths have been collected as well as simultaneous data on groundwater level and river stages, seasonal dynamics of pH, EC, ORP, temperature, and dissolved oxygen. The weather station installed by our project in the valley provides information on air temperature, precipitation, and speed and direction of wind. Selected data are uploaded to the ASCOR server and are shared with all team members.

### Task 1-2. Spatial analysis of river floodplain morphology

Spatial analysis of the floodplain morphology provides an important basis for the delineation of As contamination of soil in the Ogosta River valley. For this purpose, a digital terrain model (DTM) of the studied stretch of the valley with 1 m resolution was generated using the data obtained by the airborne laser scanning (ALS) of the study area conducted in 2013. Based on DTM analysis with SAGA free software, calculation, reclassification, and a combination of Topographic Classification Index (TCI) for lowland and Vertical Distance to Channel Network (VDCN) index was used to derive 18 representative geomorphographic units (GMUs). Following this, a map of floodplain landforms was produced in scale 1:5000 (Fig. 1a). Ground and surface laser reflection intensity maps (Fig. 1b) in ESRI and SAGA grid format and a digital surface model (DSM) of the Ogosta Valley were also generated from the ALS-data to support more adequate delineation of

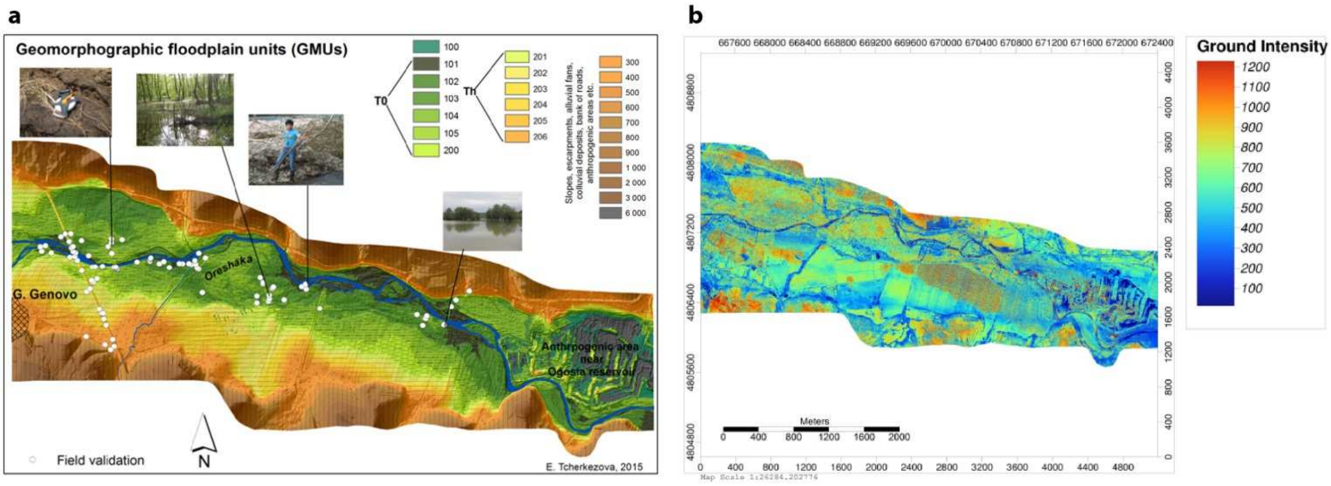


**Figure 1. (a) Geomorphographic units in the Ogosta Valley ($T_0$ – low floodplain; $T_h$ – high floodplain); and (b) Ground laser reflection intensity in the Ogosta Valley.**

the geomorphographic units and analysis of spatial distribution of As in soils. Assoc. Prof. Emilia Tcherkezova (BAS) had the major contribution to this subtask.

### Task 1-3. Hydrological analysis of the Ogosta river

Statistical analyses and calculations were made to determine the maximum values of water levels, river discharge and precipitation with different probability for past and current periods between 1950 and 2010. The biggest five flood events were selected for the period 1950-1985 when the mining in the Chiprovtsi area was the most intensive. The main characteristics of river flow peaks were estimated, e.g. magnitude and duration, to support modeling of As transport in the unsaturated zone of the Ogosta's floodplain during inundation. The hydrological analyses were performed by Assoc. Prof. Marian Varbanov (BAS).

### Task 1-4. Flood modeling

Flood modeling was performed to reveal the span of soil pollution determined by deposition of As contaminated river sediment during high flood events. The procedure followed two steps – hydrological and hydraulic modeling. The discharge of Ogosta River was simulated with the SWAT model for the floods in 1964, 1966, 1967, 1968, 1970, April and September as well as for rainfalls with return period 100, 20, 5 and 2 years. The discharge calculated for rainfalls (24h) with return period 100 years was very close to the river flow quantity with the same probability. The model was set and calibrated with precipitation and river flow data on a daily bases for the period 2000-2005. Simulations of Ogosta river's discharge were made for eight cross-sections (Fig. 2). The hydrological modelling was performed by Assoc. Prof. Stoyan Nedkov (BAS).

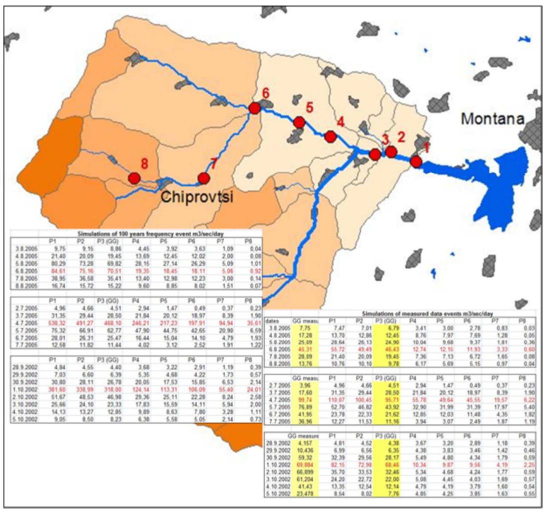


**Figure 2. SWAT simulation results of a flood event with measured data and for a flood with 100 years return period.**

Hydraulic modeling was performed with the model HEC-RAS vers. 4.1.0 for a section of the Ogosta Valley between the town of Chiprovtsi and the "Ogosta" reservoir with a length of 28.4 km. The model was calibrated with the flood event on 19.04.2014 and benefitted also from a data set of locations of inundated points that were registered in the valley after the flood. Maps of inundated areas for the selected hydrological events and return periods were produced as well as a map showing the cumulative depth of inundation of the five biggest floods during the period of the most intensive pollution of the Ogosta River (Fig. 3a). Most of the floods in the period 1964-1970 cover areas similar to these expected to be inundated by a 100 years flood (Fig. 3b) and match well with the areas of high As concentration in soil. Assist. Prof. Todor Lubenov and Senior Assist. Prof. Vladimir Kukurin (Department of Hydraulics and Hydrology, University of Architecture, Civil Engineering and Geodesy, Sofia) made the largest contribution to the hydraulic modeling.

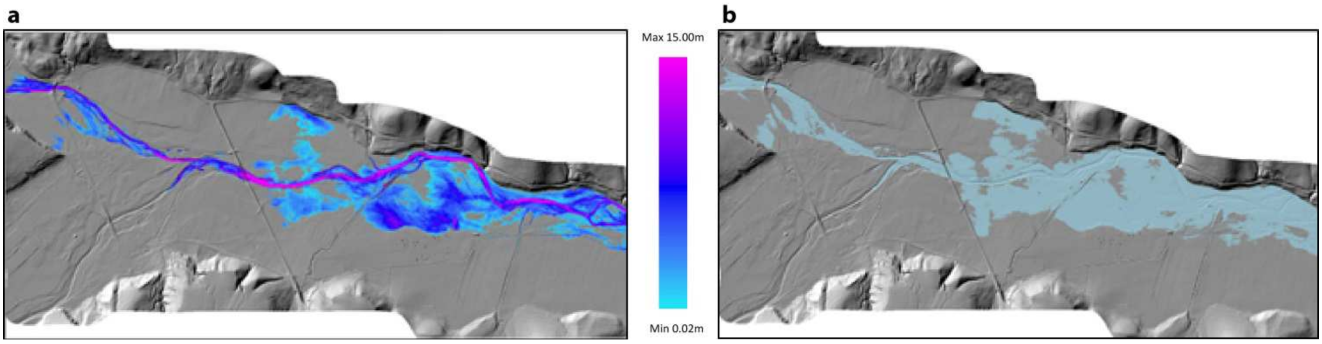


**Figure 3. (a) Cumulative depth of inundation during floods occurred in the Ogosta Valley in 1964, 1966, 1967, 1968, 1970; and (b) Simulated areas of inundation in occasions of rainfalls with a 100 year return period.**

### Task 1-5. Investigation of arsenic spatial distribution

Extensive soil sampling up to 20-40-60-80-100 cm depth was conducted within the whole studied floodplain of 1556 ha in November 2013 followed by a deep soil sampling and soil coring up to 1-5 m depth in June, August, and September 2014. The sampling concept considered the information from the floodplain morphographic analyses, the maps of floodplain geomorphographic units and from the magnetic susceptibility measurements. The field work resulted in 859 soil samples taken from 327 sites in the Ogosta Valley. Pellets have been prepared at the premises of NIGGG from all the samples and sent to ETH Zurich for measuring the concentrations of arsenic and heavy metals by XRF analyses. Arsenic was found to be in the range 9 – 29530 mg/kg with median 90 mg/kg, average 1291 mg/kg and standard deviation 3205 mg/kg. Because of the strong variation of the values, the median was preferred in our calculations with regard to As. Using SURFER 8 software, variogram analyses and kriging interpolation have been applied to generate grids 25x25 m and 50x50 m with the As concentration in soil. The latter were interpolated with the Spline method in ArcGIS and maps of As distribution in depths 0-20, 20-40, 40-60, 60-80, 80-100, and 100-150 cm were drawn (Fig. 4). The data set used for creation the grid of 0-20 cm combined ASCOR data with 271 additional records of As contents in topsoils available from a survey conducted by another research team[1] with comparable methods. The reduced number of samples in the deeper layers did not allow application of geostatistics and maps of lower depths were therefore not produced with the method described above. Nearly 1300 ha, or 84% of the studied area show As levels exceeding the Bulgarian maximum admissible concentration (MAC) of 25 mg/kg at various soil depths in the range 0-150 cm. The area with As concentrations above the intervention value of 90 mg/kg ranges between 378- 980 ha for the studied depths. The total quantity of As in the topsoil of the studied floodplain is estimated at 459 t assuming a dry soil bulk density of 1.5 g/cm$^3$ as determined for the local floodplain soil and reported in the literature for other floodplain soils. Calculations for all the soil volume from the surface to 150 cm depth estimated 3150 t of As in the Ogosta River floodplain sediment deposits. The most severely affected

[1] Spectrotech (1994). Establishment of the Type and Degree of Ecologically Polluted Farmlands with Heavy Metals in the Municipalities of Chiprovtsi and Georgi Damyanovo. Sofia (in Bulgarian).

areas are the lowest parts of the floodplain next to the river where extreme levels of contamination were found and where As often peaks in the subsoil.

A new method for modeling As distribution in floodplain soil was tested using the MAXENT software. It is mostly applied for prediction of presence of certain biological species considering spatial information on the environmental conditions. We were not able to find in the literature a survey that uses the MAXENT model for mapping of soil contamination. The model was considered appropriate for this purpose, especially for riparian areas where contamination is closely related with river floods and contaminant distribution is dependent on floodplain topography. The model was tested with 13 variables, e.g. vertical distance to channel network (VDCN), map of geomorphographic units (GMUs) of floodplain, cumulative depth of inundations in the period 1964-1970, etc., resulting in predictions for 9 intervals of As concentrations multiple of MAC named As classes, mg/kg: <25, 25-90, 90-500, 500-1000, 1000-1500, 1500-2000, 2000-2500, 2500-5000, >5000. Strong dependence of As distribution was found on the GMUs pattern, land use, soil cover, VDCN as well as on inundation depth and some other morphographic indices for certain As classes. The generated maps present similar distribution of As to this on the maps prepared with conventional geostatistical methods but much more detailed and realistic (Fig. 5). The new method shows promising results but it needs further development with regard to integration of the layers of each class into one predictive map. The main contributions to this task were accomplished by Assoc Prof. Tsvetan Kotsev (soil study and sampling concept), Dr. Velimira Stoyanova (field work and sample preparation, GIS analyses ), Assist. Prof. Todor Lubenov (MAXENT modeling), Prof. Diana Jordanova (magnetic susceptibility study), Prof. Stefan Shanov (geostatistical analysis), and Kurt Barmettler and Prof. Ruben Kretzschmar (ETH Zurich, analyses of soil samples).

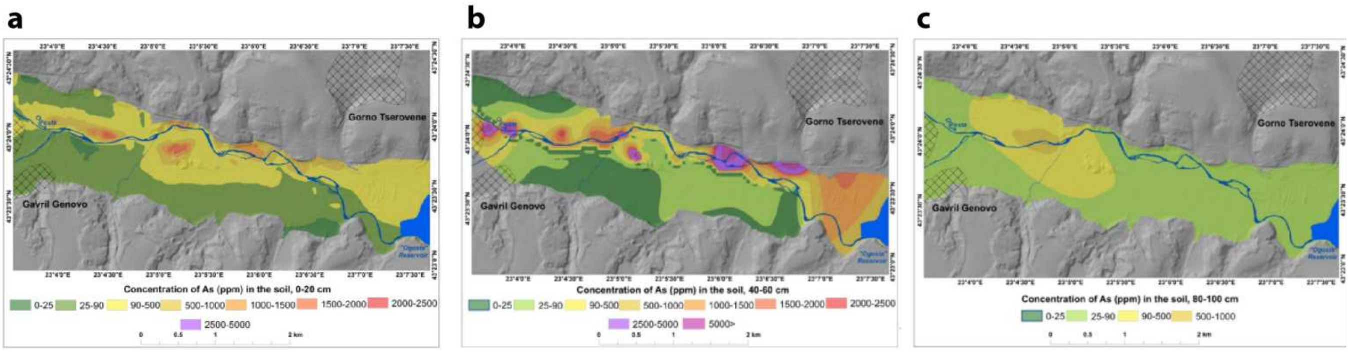


**Figure 4. As distribution in soil in the Ogosta Valley: (a) Depth 0-20cm; (b) Depth 40-60cm; and (c) Depth 80-100 cm.**

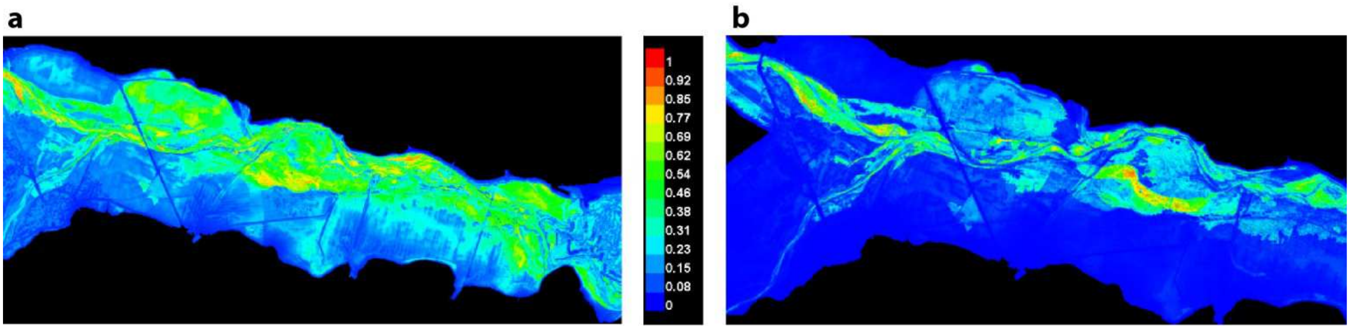


**Figure 5. Distribution of As concentrations in soil (0-20 cm depth) predicted by the Maxent model. Legend: probability of occurrence ranges between 0 and 1. (a) 1000-1500 mg/kg As; (b) >5000 mg/kg As.**

### 2.2. Results of WP2

#### Task 2-1. Analyses of soil microbial community composition and functional genes

The first objective in WP2 was to investigate As-induced changes in the soil microbial communities along a contamination gradient in the Ogosta river floodplain. To address this objective we sampled and characterized the soils along a 700 m long transect crossing the Ogosta river near Gorno Tserovene. The Fluvisols along the transect exhibited As concentrations over three orders of magnitude, ranging from 15 to 15600 mg/kg. The river banks were most severely contaminated and a decreasing trend with increasing distance to the river was observed. Taxonomic survey of the prokaryotic community along the transect revealed that the bacterial community was very diverse but dominated by *Acidobacteria* (average share of 46%). The diversity of the archaeal community was comparably low and dominated by (presumably) ammonia oxidizing species. The soil depth, a proxy for nutrient availability, and the pH were found highly predictive for the taxonomic prokaryotic community composition (Fig. 6). The As contamination apparently only has a minor influence on the taxonomic composition as assessed by the shares of higher rank taxa (phylum, class). Detailed multivariate analysis also including data on lower rank taxa is still in progress. Additionally to the taxonomic survey, we worked on analyzing functional genes. We designed, tested, and evaluated qPCR assays to enumerate prokaryotic genes encoding enzymes catalyzing As redox transformations, namely *arrA* encoding an arsenate reductase, and *aioA* and *arxA* encoding arsenite oxidases. A description of these assays will be published together with their application to samples from a sand filter for As removal from drinking water in Vietnam, which were taken as part of a project of a collaborator (Prof. Sebastian Behrens, University of Minnesota). Within the PhD project of Michael Simmler, the assays will be applied to the samples from the transect and the results related to the physicochemical characteristics of the soils. The main contributions to this task were achieved by PhD student Michael Simmler (ETH), under the guidance of Dr. Iso Christl and Prof. Ruben Kretzschmar (ETH) and in collaboration with Prof. Andreas Kappler (University of Tübingen), Prof. Sebastian Behrens (University of Minnesota), and staff of the Genetic Diversity Center, ETH Zurich.

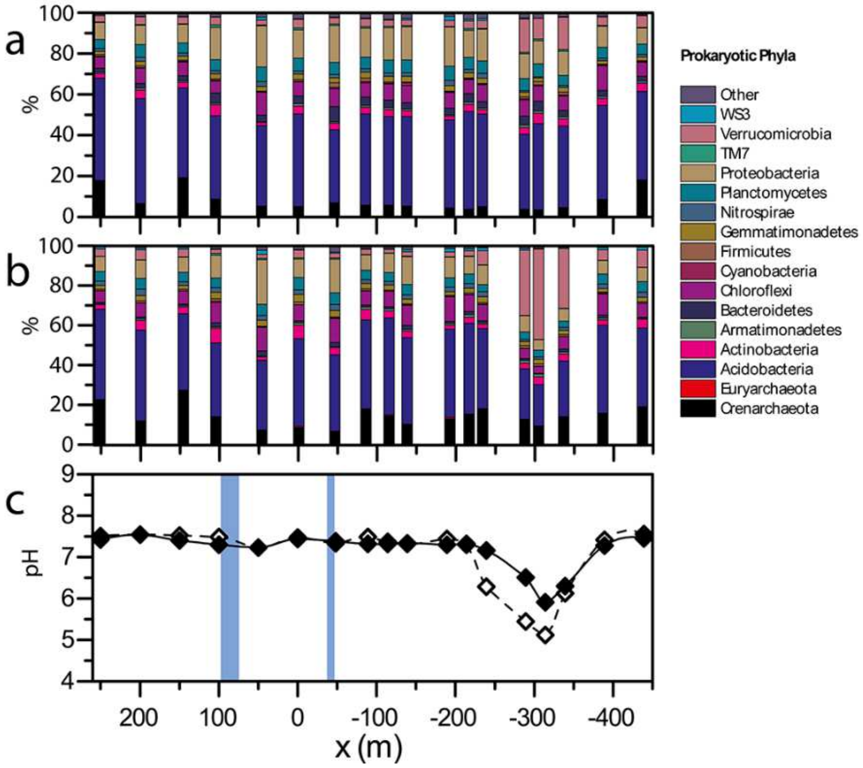


**Figure 6: Taxonomic composition of the prokaryotic communities in (a) the topsoil and (b) the subsoil, and (c) pH values at sampling locations x along the transect. The filled black diamonds (◆) represent pH values in the topsoil (0–20 cm) and the open black diamonds (◇) pH values in the subsoil (20–40 cm), respectively. The blue shaded areas indicate the approximate position of the river channels.**

**Task 2-2. Assessment of the variability of the potential microbial mobilization of arsenic from contaminated floodplain soils.**

We conducted microcosm experiments to investigate the release of As from the soil solid phase to the soil solution as a function of duration of flooding (up to 41 days), soil properties (65 different soils) and temperature (10, 17.5 and 25 °C). The set of soils included 18 soils form the transect and 47 soils from the upper Ogosta catchment between the transect close to Gorno Tserovene and the junction of Ogosta and Chiprovska river located ca. 18 km upstream. Both, chemical changes in the solid phase and the aqueous phase were monitored in the experiments. We found that the extent to which As was released from different soils varied dramatically, also between soils with similar total As concentrations. From some topsoils, very high release was observed even after short periods of flooding (1-2 weeks), while typically from subsoils the release was low even when flooded for 41 days. Figure 7 shows the soil redox potential (Eh) and the aqueous concentrations of As and Fe for incubation of 9 top- and 9 subsoils from the transect. Within the first days of flooding the soils became anoxic and reductive release of Fe and As was observed. In samples with considerable release, arsenite (As(III)) was the dominant As species. The concentration of As in solution was correlated to the concentration of aqueous Fe as shown in Figure 8ab. Using a combination of aqueous and solid phase As and Fe speciation techniques (speciation cartridge and ICP-MS, Fe and As K-edge XANES) we found that the ratio of total reduced As to total reduced Fe over 41 days of flooding is equal to the ratio of ascorbate-citrate(AscCit)-extractable As to AscCit-extractable Fe (stars on 1:1 line in Figure 8c). Apparently the reduction/release of As was coupled to the reduction of the AscCit-labile Fe which represents the Fe pool present as poorly crystalline iron hydroxide phases. This microbially reactive, AscCit-labile Fe pool is only a minor fraction of the total Fe in the soils from along the transect, but is enriched with As as compared to the bulk soil (<10% of total Fe and up to 60% of total As).

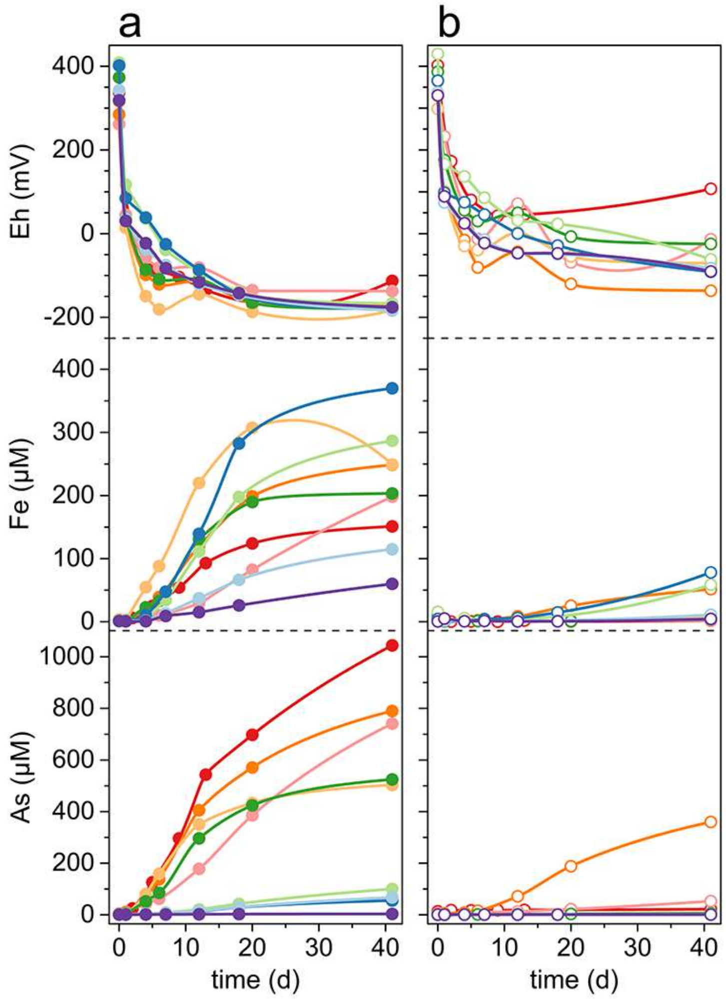


**Figure 7: Temporal dynamics of the soil redox potential Eh and the total aqueous concentrations of Fe and As for the microcosm incubations of (a) topsoils (b) subsoils from the transect.**

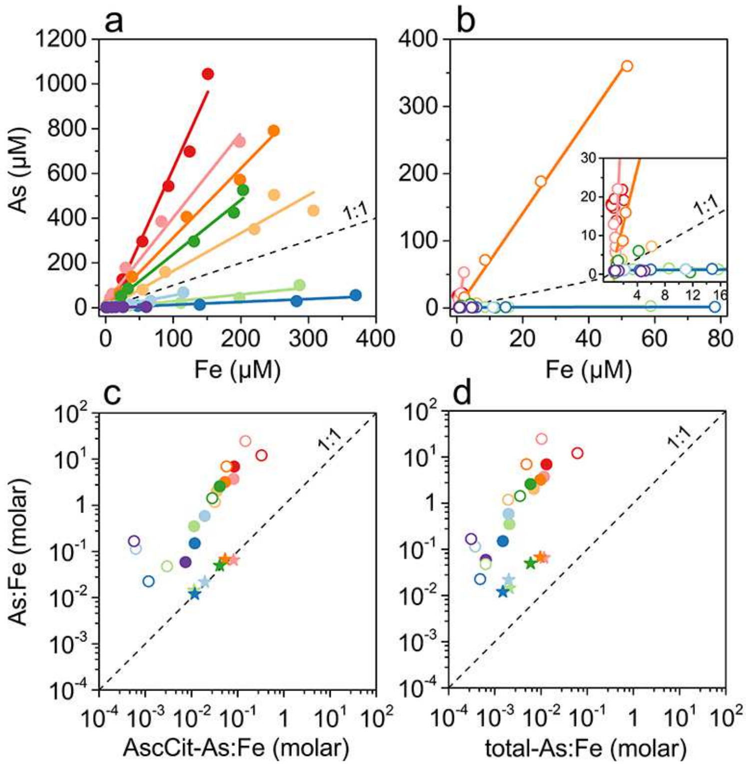


**Figure 8: Total aqueous As concentration plotted against the total aqueous Fe concentration for the microcosm incubations of (a) the topsoils and (b) the subsoils from the transect. Panels (c) and (d) show molar As:Fe ratios for total aqueous concentrations at day 41 of incubation (circles), and for the amounts of As and Fe reduced during the 41-day incubation (stars) plotted against (c) the molar As:Fe ratio for the ascorbate-citrate extractable concentrations, and (d) the total solid phase concentrations. Symbol and line colors correspond to Figure 7; filled and open symbols represent top- and subsoils, respectively. Solid lines in (a) and (b) represent orthogonal regression lines. The reduced As and Fe in (c) and (d) was calculated considering both the solid and the solution phase speciation.**

By conducting correlation and best subset multivariate linear regression analysis we explored the dependencies of the As release on the soil's properties. The dataset consisted of 65 observations or different soils, respectively. All soils were incubated in microcosms for 20 days and the As released to the soil solution was determined. This release data was related to comprehensive physicochemical soil characterization data in order to identify potential drivers and inhibitors. The availability of nutrients (org. C, N) was found to highly limit the release of As. Also high manganese contents apparently inhibit the release, presumably by (i) Mn(III/IV) respiration competing with Fe(III) and As(V) respiration and/or (ii) Mn(III/IV) oxides reoxidizing Fe(II) and provoking the precipitation of As-sequestering ferrihydrite. The best 3-variable multi-log-linear model [Eq. 1] included N, AscCit-extractable As, and AscCit-extractable Mn as explanatory variables. It explained 80% of the variance in the decadic log of the aqueous concentration of As ($\log_{10}(As_{dis})$), whereas a log-linear model with only total As explained only 15%.

$$\log_{10}(As_{dis}) = 1.055 + 1.461 \log_{10}(\text{total N}) + 0.896 \log_{10}(\text{AscCit-As}) - 2.297 \log_{10}(\text{AscCit-Mn}) \qquad \text{[Eq. 1]}$$

units: $As_{dis}$ in μM, all other in mmol/kg; $R^2$=0.8

The 18 soils used for the experiments discussed in Figure 2 and 3 were also used for microcosm experiments run at different temperatures in order to determine the temperature dependence of As release. The results are shown in Figure 9. In soils with considerable release, the temperature dependence expressed as temperature coefficient $Q_{10}$ varied between 2.3 and 6.1. This is of similar magnitude as found in the literature for other soil processes related to anaerobic respiration, e.g., methane emission from wetlands ($Q_{10}$ values 2.5 - 5.9). A manuscript summarizing all results from our microcosm experiments is currently in preparation. It will be submitted to the journal *Environmental Pollution*.

The results of the microcosm experiments have important environmental implications. Despite the subsoils being most contaminated, the release of As from these soil layers during water saturated conditions is limited by low nutrient availability. In contrast, the less polluted topsoils possess a higher potential to reductively release their arsenic to the soil solution as nutrients and carbon sources to drive anaerobic microbial respiration are abundant. Water saturation of subsoil layers as a result of rising groundwater table might therefore be regarded less problematic than surface flooding. Agricultural practices which result in enhanced contact of nutrients and As contaminated soil material should be avoided. These include the application of fertilizer or

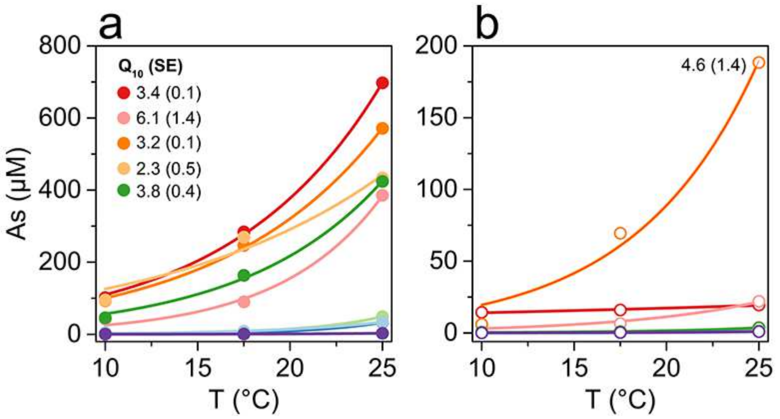


**Figure 9: Temperature dependence of the aqueous As at day 20 of incubation for (a) the topsoils and (b) the subsoils from the transect. Colors correspond to Figure 1. The $Q_{10}$ temperature coefficient and the standard error from curve-fitting are reported for the soils with considerable As release ($Q_{10}$ determined by fitting As(µM)~a*$Q_{10}$^(T (°C)/10)).**

deep plowing (mixing nutrient-rich top- and highly contaminated subsoil material). The Ogosta floodplain is typically flooded in spring to early summer as a result of snow melt in the Balkan Mountains, or in winter as a result of heavy rainfall. The high temperature dependence of As release implicates that not only the duration of flooding but also the time of the year, during which a flood occurs, is of crucial importance when it comes to estimating a flood's potential to induce reductive release of As from soil. Considering this, the floods in early summer might bear the highest risk.

In a related study (Dr. Elke Suess, DFG Postdoctoral Fellow, ETH), data on As and P concentrations in three pasture plant species (*H. lanatus*, *A. spica-venti*, *T. repens*) growing along the above mentioned transect was studied. We related her plant uptake data to the soil characterization data obtained within this project in order to investigate the soil-to-plant transfer of As and P. Figure 10 shows selected results concerning As in soil and shoots of *H. lanatus*. We found that the As contamination gradients in the soils (Fig. 10a) were reflected in the As plant concentrations (Fig. 10b), but that transfer was restricted with transfer factors mostly below 0.07 ($TF=As_{shoot}/As_{soil}$). Compared with literature data, the soil-to-plant transfer factors were relatively low (Fig. 10c). Considering typical involuntary soil ingestion by livestock, we suggest that for livestock grazing along the transect or on similar contaminated parts of the floodplain, intake via soil ingestion might be even more important than intake via pasture herbage. A manuscript documenting this field survey was submitted to the journal *Science of the Total Environment*. The main contribution to this task was achieved by PhD student Michael Simmler (ETH) under the guidance of Dr. Iso Christl and Prof. Ruben Kretzschmar (ETH). Prof. Tsvetan Kotsev and team members helped with field work and provided additional samples.

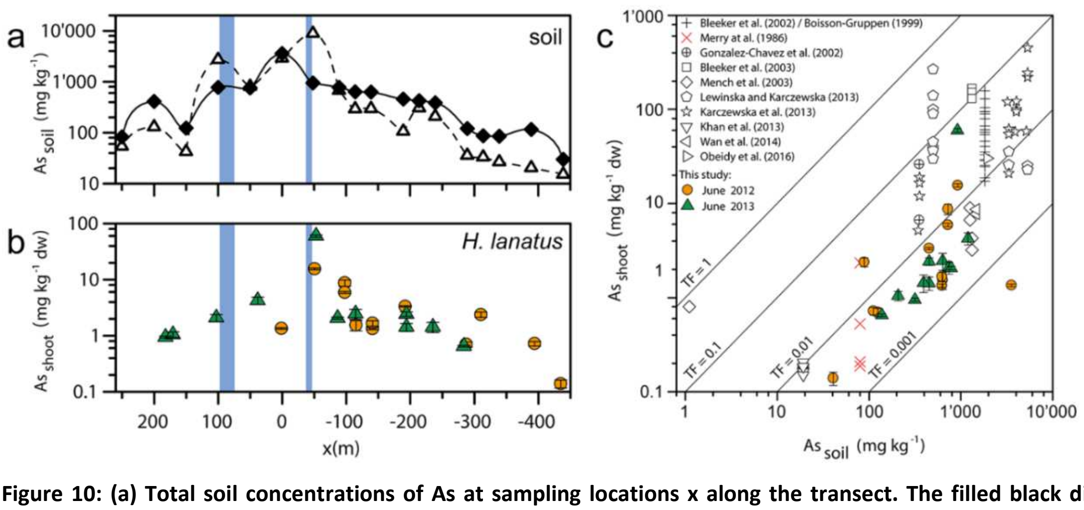


**Figure 10: (a) Total soil concentrations of As at sampling locations x along the transect. The filled black diamonds (◆) represent topsoil (0–20 cm) concentrations and the open black diamonds (◇) subsoil (20–40 cm) concentrations, respectively. The blue shaded areas indicate the approximate position of the river channels. (b) Concentrations of As in shoots of *H. lanatus* at sampling locations x along the transect. Orange circles (●) and green triangles (▲) represent samples collected in year 2012 and 2013, respectively**

## 2.3. Results of WP3

### Task 3-1. Assessment of arsenic fluxes via groundwater

A system of 23 tube wells was constructed in the Ogosta Valley in June to September 2014 to provide monitoring of groundwater. Two wells and a river monitoring site along a cross section were equipped with automatic telemetric systems for measurements of water level, temperature, EC, pH, ORP, and dissolved $O_2$ for better understanding the interactions between the river flow and groundwater and As mobilization and transport. Water sampling and measurements of physicochemical parameters started on a monthly basis since November 2014, though many of the wells have been monitored even earlier. Within the project life time about 330 river water and groundwater samples in three replicates have been collected and sent to ETH Zurich for chemical analysis and measurement of As and heavy metals with ICP-OES and ICP-MS. Separation of As(III) from As(V) has been performed in the field using speciation cartridges (MetalSoft Center, USA) filled with material which selectively adsorbs As(V) while As(III) passes through and is measured as total As in the sample by ICP-MS. Most samples show arsenic concentrations higher than the MPL for drinking water (>10 µg/L) and in many cases the threshold for irrigation water was also exceeded (>100 µg/L). The highest contaminant levels are associated with the wells in the lowest parts of the floodplain where the soil was highly polluted and the groundwater vulnerability to As contamination was determined to be very high (Fig. 11). Arsenic levels in groundwater are near the threshold for drinking water in the higher floodplain with less contaminated soil. Results did not a show correlation between changes in groundwater level and As concentration in the water samples (Fig. 12). It is worth noting that the peak of arsenic in the most of the wells was registered after the big flood in September 2015, but the impact of such events on As release from soil to groundwater requires additional studies under high flow conditions.

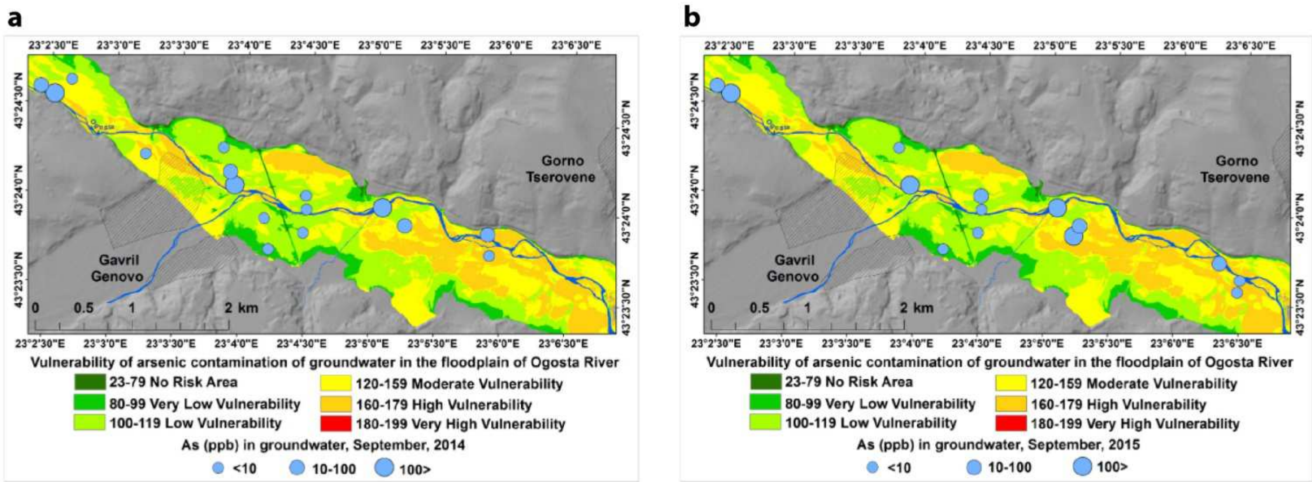


**Figure 11. As (ppb) in groundwater: (a) High GW table after flood in Sept 2014; (b) Low GW table in Sept 2015.**

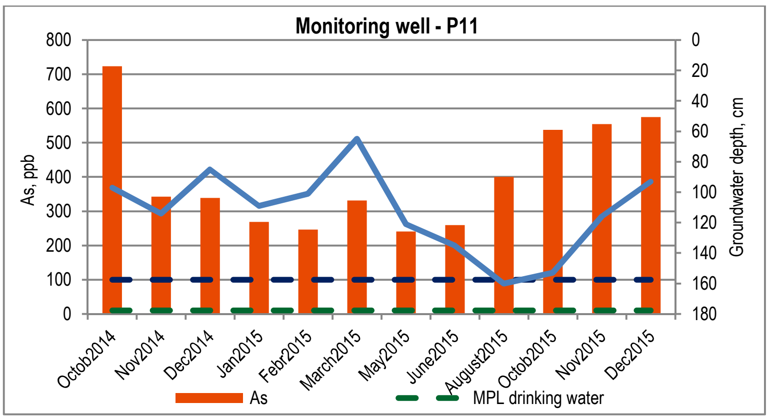


**Figure 12. Seasonal changes of As concentrations versus groundwater level dynamics in one of the monitoring wells (P11).**

Modeling of As transport in the vadose and saturated zones of the Ogosta river floodplain were performed with HYDRUS1-D, MODFLOW and MT3DMS software for 18 and 12 sites, respectively. As(V) was assumed to be the prevalent species compared with As(III) in the well oxidized, unsaturated alluvial deposits above the groundwater table. A good correspondence of the rainfalls and water fluxes through the profiles were shown. The concentration of As in solution phase was assumed to be coupled to that in the solid phase through Kd values determined by laboratory experiments conducted at ETH. Assuming oxic conditions in soils, As from contaminated layers was not predicted to migrate much to layers beneath (Fig. 13). The total inflow of groundwater in the area between the village of Beli mel and the „Ogosta" reservoir amounted to 22.67 L/s and its significance in deposition and dissolution of the pollutant in the saturated zone was predicted to be negligible. A major role the in spreading of arsenic in the alluvial terrace must thus be attributed to the river water. Since As(III) was well presented together with As(V) in many groundwater samples, it was preferentially modeled in the saturated zone because of its higher mobility compared with As(V). The trivalent species of As was predicted to travel in the aquifer over a distance of 100 m to Ogosta River within 14, 5 and 5 years, respectively for the selected sites near Belimel, Gorna Kovachica, and Gavril Genovo, while As(V) was predicted to move only a few meters within a period of 25 years (Fig. 14). This task was accomplished by Assoc. Prof. Tsvetan Kotsev (design and construction of the groundwater monitoring net, water sampling), Prof. Aleksey Benderev (hydrogeological settings, design of the monitoring wells), Dr. Velimira Stoyanova (groundwater vulnerability map, water sampling, GIS analyses), Dr. Nathalie Van Meir (modeling of vertical water flow in vadose zone), Dr. Dimitar Antonov (modeling of As transport in vadose zone), Assist. Prof. Petar Gerginov (modeling of As transport in saturated zone), Ivan Petkov (water sampling), and Kurt Barmettler, Michael Simmler, Dr. Iso Christl, and Prof. Ruben Kretzschmar (ETH Zurich, analysis of water samples, determination of Kd values for As(III) and As(V)).

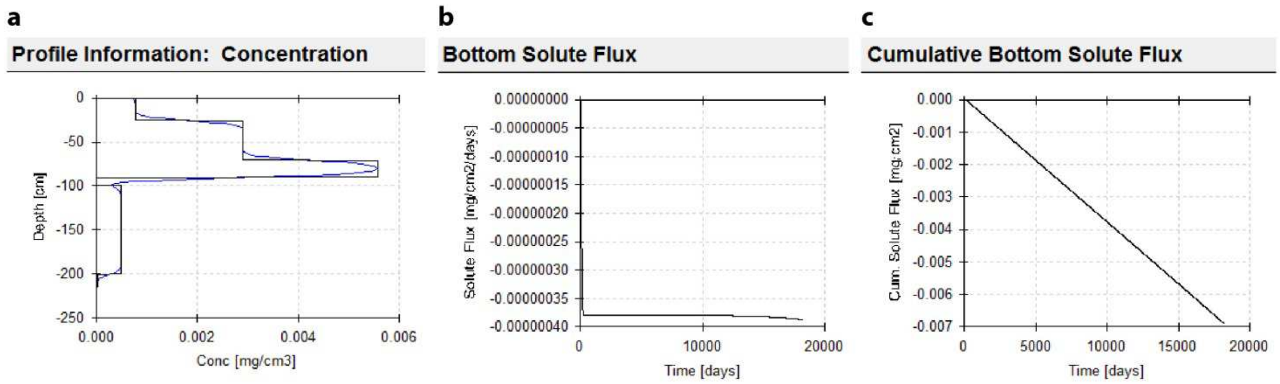


**Figure 13. Transport of As V down the highly contaminated soil profile of monitoring well No 6 for a period of 50 years.**

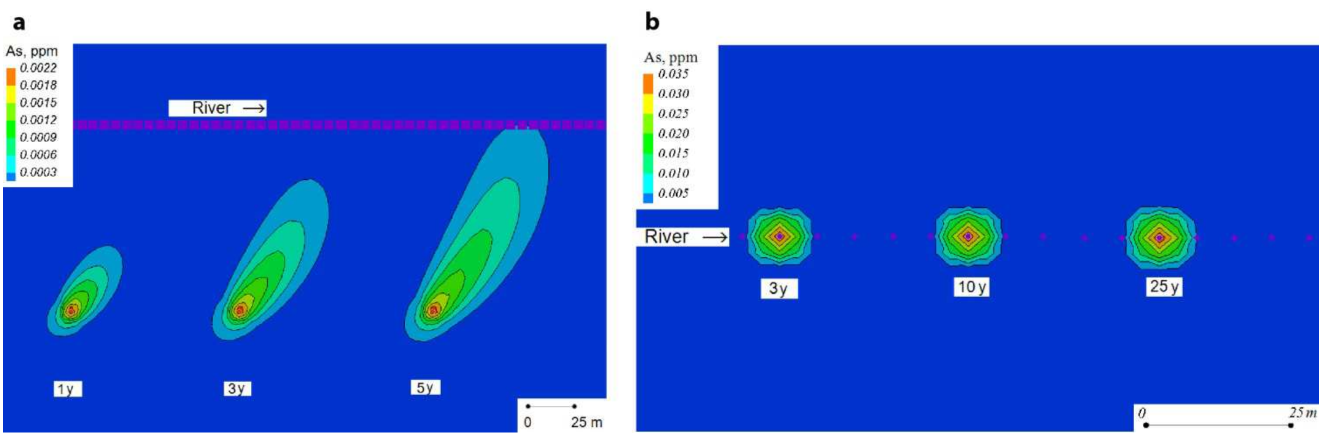


**Figure 14. Transport of (a) As(III); and (b) As(V) in the saturated zone of the Ogosta's floodplain near.**

**Task 3-2. Assessment of arsenic fluxes in the Ogosta river**

Arsenic fluxes in the Ogosta river are mostly dependent on contaminant concentrations in the river water and particulate matter. River monitoring was performed at three sites along the main river: R1- in the uppermost stretch upstream the Fe-mines; R2 – downstream the mining area; R3 – mouth of Ogosta River into the "Ogosta" reservoir at the outflow of the studied river basin. The mean river discharge in each of the three cross sections was determined for a longer period using available data on the module surface runoff. It was estimated at 0.255, 1.875 and 6.171 $m^3/s$ for R1, R2, and R3, respectively. The average concentration of dissolved As in river water samples taken in the period Dec2013 –Dec2015 amounts at 3.075 µg/L for R1 (22 samples), 74.106 µg/L for R2 (25 samples) and 45.412 µg/L for R3 (26 samples). The annual flux of dissolved As with the Ogosta river water was estimated for the three river monitoring sites at 25 kg at R1, 4382 kg at R2, and 8837 kg at R3. The average quantity of particulate matter in the river water ranges between 32-86 $g/m^3$ for the three river cross-sections in 2014 and 2015. The annual discharge of particulate matter is estimated at 424 t in 2014 and 362 t in 2015 for R1, 5064 t/ 3376 t for R2, and 6310t/11118 t for R3. There is no data on As content in particulate matter of river water and this was the reason to take the average As concentrations of couples of overbank sediment samples taken at each river monitoring site at medium and high river stages. The annual As fluxes with particulate matter are approximately 34.5 kg in 2014 and 29.5 kg in 2015 for R1, 8951 kg/5964 kg for R2 and 4686 kg/8257 kg for R3. The results show rather equal distribution of As fluxes between solute phase and particulate matter.

This task was accomplished by Assoc. Prof. Tsvetan Kotsev and Ivan Petkov (water sampling, flow measurements, flux calculations), Assoc. Prof. Marian Varbanov (hydrologic analysis) and Kurt Barmettler and Prof. Ruben Kretzschmar (ETH Zurich, Analysis of water samples).

## 3. Deviations from research plan

No significant deviations from the research plan occurred.

## 4. Collaboration aspects

The contributions of the team members including collaborators have been mentioned at the end of each task section.

Several joint field trips were organized in June 2013, May 2014 and 23-26 February 2015. The purpose of the first trip was collecting samples from soil, plants and river water to study arsenic fate in the river floodplain. Ruben Kretzschmar, Tsvetan Kotsev, Kurt Barmettler, Michael Simmler, Elke Suess, Katrin Ehlert, Stoyan Nedkov, Aleksey Benderev, Velimira Stoyanova and Kremena Boyanova took part in the survey. The second field trip aimed at assessment of short term dynamics of arsenic in the Ogosta River and high frequency sampling of river water was accomplished. This work involved Ruben Kretzschmar, Tsvetan Kotsev, and Kurt Barmettler. Collecting samples from river water and groundwater within the monitoring programme, as well as from soil for laboratory experiments at ETH-Zurich was performed by Tsvetan Kotsev, Todor Lubenov, Ivan Petkov and Katrin Ehlert and during the last joint field trip.

A project workshop was held in May 8-9, 2014, at BAS. The workshop included presentations by several members of BAS and ETH and in-depth discussions on data integration and future work.

Tsvetan Kotsev and Velimira Stoyanova visited the Soil Chemistry Group headed by Prof. Ruben Kretzschmar at ETH-Zurich in November 1-6, 2015, for discussions of the obtained project results and for planning joint publications.

## 5. Research output

**Publications:**

Mikutta, C., Mandaliev, P.N., and Kretzschmar, R. (2013): New clues to the local atomic structure of short-range ordered ferric arsenate from extended X‑ray absorption fine structure spectroscopy. *Environ. Sci. Technol*. 47, 3122−3131.

Tcherkezova, E. (2015). GIS-based delineation and regionalisation of geomorphographic units in the floodplain of Ogosta River between the settlement Gavril Genovo and the "Ogosta" reservoir (NW-Bulgaria). *Problems of Geography*, issue 1-2, BAS, Sofia.

Stoyanova, V. (2015). Variables for groundwater vulnerability assessment from arsenic contamination in the Ogosta River floodplain between the village of Martinovo and the „Ogosta" dam lake. *Problems of Geography*, issue 3-4, BAS, Sofia.

Benderev, A., Gerginov, P., Antonov, D., Meir, N.V., Kretzschmar, R. (2015). Conceptual hydrogeological model of the Ogosta river floodplain (Western Balkan, Bulgaria) and its application for predicting groundwater contamination with arsenic. Proceedings of SGEM Conference, June 18-24, 2015, res. Albena, Bulgaria.

Antonov, D., Hristov, V., Benderev, A., Kotsev, T. (2015). Comparing the parameters from pedotransfer functions and in situ permeability tests in the vadose zone of the Ogosta River floodplain in connection with validation procedures of contaminant migration modelling. Proceedings of the National Conference with international participation "GEOSCIENCES 2015", December 10-11, 2015, Sofia, Bulgaria, p. 139-140, ISSN 1313-2377.

**Planned publications:**

Simmler M, Suess E, Christl I, Kotsev T, Kretzschmar R.: Soil-to-plant transfer of arsenic and phosphorus along a contamination gradient in the mining-impacted Ogosta River floodplain. Manuscript submitted to *Science of the Total Environment*.

Simmler, M., Bommer, J., Frischknecht, S., Christl, C., Kotsev, T., and Kretzschmar, R.: Solubility of As during flooding of a mining impacted floodplain: Dependence on duration of flooding, soil properties and temperature. Manuscript in preparation (to be submitted to *Environmental Pollution*).

Simmler, M., Behrens, S., Christl, I., Kotsev, T., and Kretzschmar, R.: Soil prokaryotic community along an arsenic contamination gradient in a mining-impacted floodplain: Taxonomic composition and abundance of arsenic metabolism genes. (manuscript to be prepared)

Antonov, D., Gerginov, P., Meir, N., Benderev, A., Simmler, M., Christl, I., Kretzschmar, R., and Kotsev, T.: Arsenic transport in the vadose zone and in alluvial aquifer of contaminated river floodplain. (manuscript to be prepared)

Kotsev, T., Stoyanova, V., Tcherkezova, E., Shanov, S., Christl, I., Simmler, M., Jordanova, D., Kretzschmar, R.: GIS-based analysis of arsenic spatial distribution in soils of the Ogosta Valley against river dynamics, floodplain morphography and land use. (manuscript to be prepared)

Lubenov, T., Stoyanova, V., Tcherkezova, E., Nikolov, K., Kretzschmar, R., and Kotsev, T.: Application of MAXENT modelling for prediction of contaminant distribution in floodplain soil. (manuscript to be prepared)

Stoyanova, V., Benderev, A., Lubenov, T., Barmettler, K., Kretzschmar, R. and Kotsev, T.: GIS-based analysis of arsenic spatial distribution and dynamics in groundwater of the Ogosta Valley against floodplain morphography. (manuscript to be prepared)

Stoyanova, V., Benderev, A., Simmler, M., Tcherkezova, E., Ehlert, K., Nikolova, M., Barmettler, K., Kretzschmar, R., and Kotsev, T.: An integrated GIS-based approach to groundwater pollution risk assessment in arsenic contaminated river floodplain (Michi's and Katrin's results can be used here). (manuscript to be prepared)

**Scientific Presentations:**

Kotsev, T.: NIGGG-BAS Seminar: Mining impact to the Riverine Environment in Bulgaria – Geoecological Issues Related to Ogosta River Valley. Bulgarian Academy of Sciences, Sofia, Bulgaria, June 8, 2012 (workshop organized during the preparation phase of the project).

Kretzschmar, R.: NIGGG-BAS Seminar: Micro-XRF/XAS studies on arsenic speciation in Ogosta floodplain soils. Bulgarian Academy of Sciences, Sofia, Bulgaria, June 8, 2012 (workshop organized during the preparation phase of the project).

Kretzschmar, R.: Speciation and mobility of trace elements in wetland soils. Goldschmidt Conference, August 25-30, 2013, Florence, Italy (invited keynote presentation).

Stoyanova, V.: Variables for groundwater vulnerability assessment from arsenic contamination in the Ogosta River floodplain between the village of Martinovo and the „Ogosta“ dam lake. Scientific Conference in memoriam of Prof. Batakliev, October 30-31, 2014, Pazardzhik, Bulgaria.

Kretzschmar, R.: Speciation and biogeochemical cycling of As in periodically flooded soils affected by redox processes. Invited talk at Nanjing Agricultural University, China, March 2015.

**Public Outreach**

**Chiprovtsi townhall meeting, April 9, 2013.** *Objective:* Presentation of the project goals and activities to local authorities and governmental agencies, local companies, and NGOs. *Participants:* Vice-Mayor of Municipality of Chiprovtsi, Mayors of villages in the Ogosta Valley, representatives of the Executive Agency for Fisheries and Aquaculture, residents of Chiprovtsi. *Outcome:* Dissemination of information about the project ASCOR among the local communities and authorities; gained support and positive attitude of local administration and people to the ASCOR project; signed cooperation agreement between NIGGG-BAS and the Mayor of Chiprovtsi to support ASCOR project activities. *Speaker:* Prof. Tsvetan Kotsev.

**Field demonstration for pupils from a local school, June 6, 2013.** *Objective:* Explain and demonstrate ASCOR project activities to pupils in the field (Figure 15). *Participants:* 25 pupils, a teacher, and the Headmaster of the school Petar Parchevich in Chiprovtsi. *Outcome:* Increased awareness of young local people about the risks and hazards from the arsenic pollution in the Ogosta Valley, dissemination of information about the ASCOR project in the local communities. *Speaker:* Prof. Tsvetan Kotsev; with demonstration of water sampling techniques by Prof. Ruben Kretzschmar and Kurt Barmettler (ETH).

**Figure 15: Demonstration of soil sampling with a drill auger to pupils from a local school in Chiprovtsi.**

**Automatic meteorological station** is installed in the lands of EcoTerra organic farm in the Ogosta Valley and the real time weather information is used by the agronomists for short term planning of farming activities.

**Talks and explanations of environmental risks** related with As contamination were given to the local people in the field during the construction works of the groundwater monitoring system in June-September 2014.

## 6. Further use of equipment

A public procurement procedure has been completed by the Bulgarian PI in order to purchase the following equipment for ground water and river water quality monitoring at a total price of 41775.75 CHF:

- LogCom-2/GSM/MPS-PTEC, SEBA Hydrometrie (Germany), 2 pieces – automatic telemetric system for measurement of water level, temperature and electric conductivity installed in a monitoring well (No P14) and in the Ogosta River’s channel (No P13R);
- LogCom-2/GSM/MPS-D8, SEBA Hydrometrie (Germany), 1 piece – automatic telemetric system for measurement of water level, temperature, electric conductivity, pH, redox potential (ORP), dissolved oxygen, installed in a monitoring well (No P14) in the Ogosta Valley;
- KLL-Q-2 MPS-D8, SEBA Hydrometrie (Germany), 1 piece – a system for field measurement of water level, temperature, electric conductivity, pH, redox potential (ORP), dissolved oxygen, which is used for water monitoring of all the tube wells and river sites in the Ogosta Valley;
- GEOCONTROL PRO, Geotech Environmental Equipment (USA), 1 piece – a device especially designed for sampling groundwater from tube wells.

All the equipment is stored at the premises of NIGGG-BAS in complete order. It will be used for groundwater and river water quality monitoring in the Ogosta Valley, which will continue at least for two more years after the end of ASCOR project. The aim of the further water monitoring will be to reveal the impact of river floods on arsenic fluxes from contaminated floodplain soil to groundwater and river.