Chemical, Physical and Diatom Analyses of Rivers in North West Greece

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WTW's collaboration with the Limnological Institute of the TU München (Munich Technical University) has enabled a doctoral candidate to ecologically assess selected running waters in Greece by comparing the water quality with corresponding rivers in Bavaria. Diatoms, a photo-synthetic algae with cell walls composed of glass, were identified from three rivers in the north west of Greece (Epirus). In addition chemical and physical properties of the water were also recorded. A secondary goal of the project was to discover the source of suspected pollutants. The investigation was intended to serve as the initial step for the implementation of the European Water Framework Directive. The EWFD states that all waters in the EU exhibit a 'good' ecological condition by 2015. To determine the current ecological status, diatoms, long recognised as useful and accurate bio-indicators, were used.

Figure 1: Discharge of Ioannina wastewater channel

Epirus is the most north westerly of the 13 regions in Greece and has an area of 9223 km² and 353,820 inhabitants.
The Pindos mountain range runs north - south through the entire region such that 74% of Epirus is in the montane zone. This mountain range is responsible for the high level of precipitation generated in this region. Moisture-laden clouds from the west deposit rain before crossing the summits. Because of this, numerous watercourses flow to the west, draining into the Ionian sea. Until now, there has been little in the way of chemical and ecological characterisation of this rivers.

The four main watercourses in Epirus originating in the Pindos mountain range are Arachthos, Kalamas, Acherontas and Louros. The first three were analysed within the presented study by scientists of the Limnological Institute of the TU München. The example described in this article provides a report on just one of the rivers, the Kalamas.

The Kalamas river is approximately 115 km long and has a catchment area of 1747 km². It begins north of the capital city Ioannina near to Kalpaki and flows out into the Ionian Sea (see Fig. 3). Numerous tributaries feed the main river, of which the six largest streams, Gormos, Tiria, Zalogitikos, Smolitsas, Kosovitikos and Kalpakiotikos, were involved in this analysis.
In addition to these natural tributaries, an important man-made tributary was also included, the outflow from the Ioannina's wastewater treatment plant (Fig.1). The city has approximately 100 000 inhabitants and is situated on the banks of Lake Pamvotis. For centuries Lake Pamvotis was polluted by the city's wastewater. To prevent further pollution, a wastewater treatment plant was built. Today, the outflow of the wastewater treatment plant passes into a receiving water approximately 10 km long. It then joins the Smolitsas tributary, eventually flowing into the Kalamas river. The figure 1 shows the wastewater before it reaches the receiving water. The river is often negatively reported in the press, because of the outflow from the wastewater treatment plant of Ioannina. Diatom analysis conducted in this study, with the aid of physical measurements and chemical analyses with WTW instruments, made it possible to determine whether this discharge pollutes the Kalamas ecosystem.

The sampling procedure and the chemical analyses were carried out over a period of two years. A total of 28 sampling points were visited along the Kalamas watercourse system. At each sampling point, water and diatom samples were taken, the physical parameters were measured, and the local conditions were also documented. The "Multi 350i" multi-sensor from WTW was used in measuring the physical parameters (Fig. 2).
This instrument allowed to measure directly oxygen saturation (%), oxygen content (mg/l), conductivity (µS/cm), acidity (pH values) as well as the air and water temperature (°C) both quickly and accurately.

Chemical analyses of the water samples were performed by photometric determination, using the "photoLab® S12" cuvette photometer from WTW and "Spectroquant®" cuvette tests from Merck and WTW.
All tests were carried out as described in the manufacturer's manual, requiring only 50 ml of water and were carried out in a short space of time.
The following key chemical parameters were analysed: total phosphorus (TP), soluble reactive phosphorus (SRP), ammonium nitrogen (NH_4–N), nitrate nitrogen (NO_3–N), total hardness, silicon (Si), sulphate (SO_4^{2-}) and chloride (Cl^-). Prior to determining the

Figure 2: Multi 350i multiparameter instrument from WTW

total phosphorus content, the samples were digested with the aid of the "Crack Set 10" from Merck and the "CR 2200" thermoreactor from WTW. All measured extinction values were automatically converted and reported by the photometer as concentrations (mg/l).

The more relevant results from the physical and chemical analyses of the 10 sampling sites along the main Kalamas river are presented here.

The temperature of the Kalamas river (Fig.5) increased continuously along its course from about 13°C at the source to 17°C at the estuary.
The temperature progression reflects the classic progression in rivers where cold spring water warms along the length of a river. With 1733 µS/cm at the source, conductivity received comparatively high values.
In contrast to the temperature, along its course conductivity values declined to an average of about 600 µS/cm. The higher values in the upper reaches can be attributed to the geologically-related high sulphate concentrations in the groundwater.
The conductivity of 1414 µS/cm which was measured at the estuary is clearly reflecting the tidal influence of the Ionian Sea that flows into the river. The pH values along the entire river system were just above 8.0, which is typical for water that flows through limestone.

The oxygen saturation (Fig.6) and the oxygen concentration provide a similar picture, with low values of 64.0 % or 6.22 mg/l respectively measured at the source of the river which slowly rose as the distance from the source increased. Low oxygen saturations are expected in source regions. Due to the long period that groundwater remains in the ground until it emerges at the source, the oxygen supply of the groundwater is consumed by microbiological degradation processes. This process leads to the oxygen deficiency of the groundwater or of spring water that are expressed in terms of under-saturation.

The chemical analyses (Fig. 7 and 8) confirm the feared negative effect of the wastewater fed into the watercourse. The total phosphorus values were approximately 0.024 mg PO_4^{3-}-P/l up to the sampling point prior to the confluence of the Smolitsas tributary. From the first sample after the tributary (sampling point 5), phosphorus concentrations increased almost six-fold. The microbial activity of the river did, however, decrease the phosphorus concentrations along its course. A comparable effect was also demonstrated by the dissolved phosphate, nitrate, and ammonia concentrations using WTW instruments.

For the diatom analyses stones were taken, from the riverbed and the slimy coating (aufwuchs) of the stones was brushed off and collected. The aufwuchs primarily consists of microscopic small diatoms that have a brownish colour due to their photosynthetic pigment (Fucoxanthin).

Figure 4: Diatom

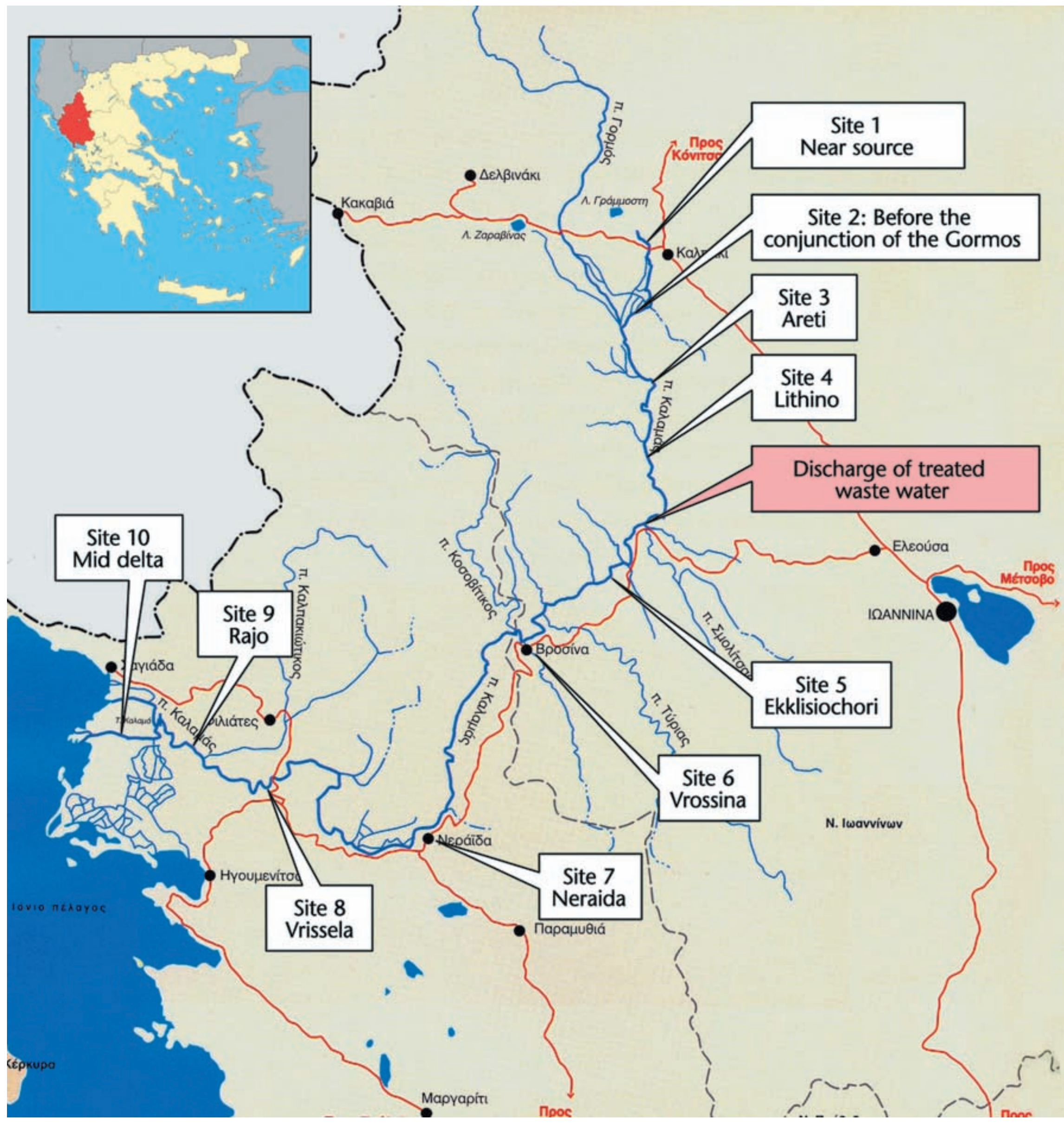

Figure 3: The Kalamas river with the sample points

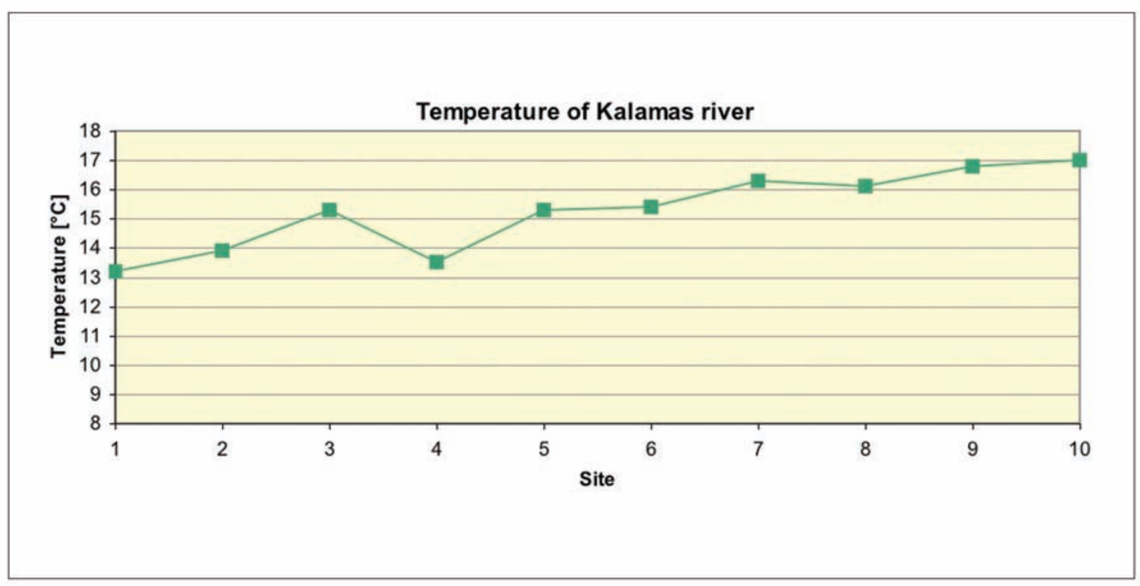

Figure 5: Temperature of Kalamas River

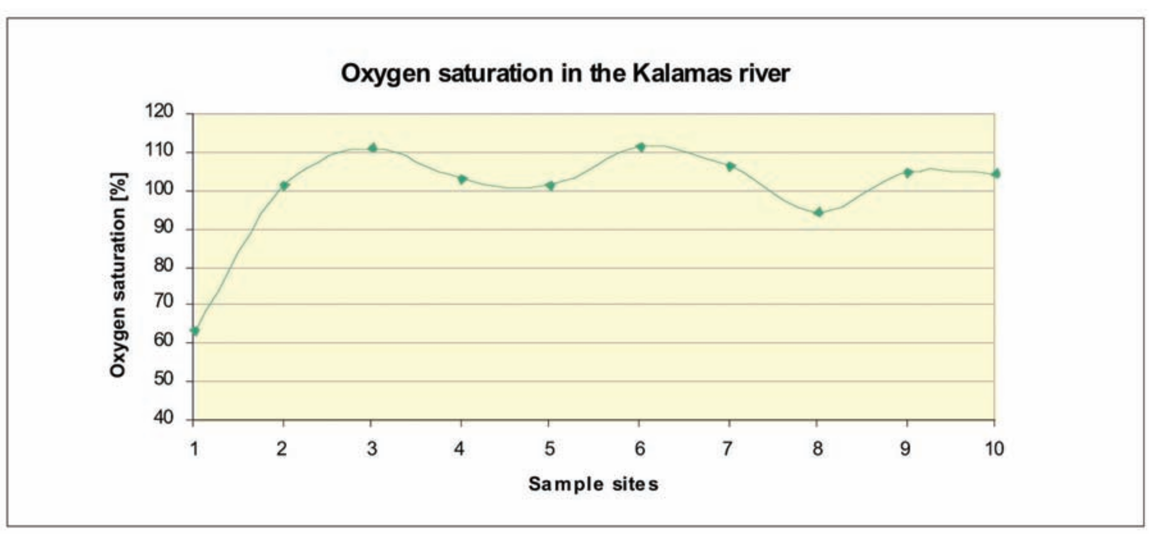

Figure 6: Oxygen Saturation in the Kalamas River

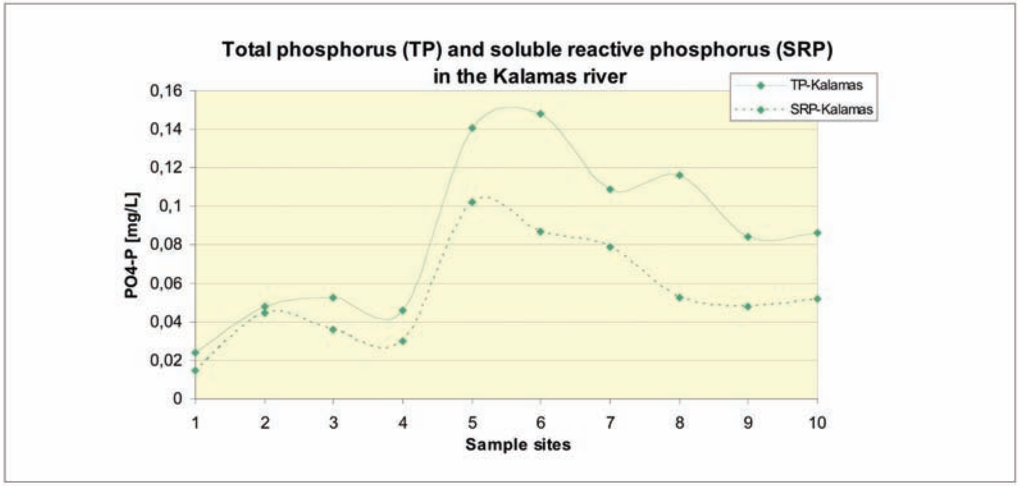

Figure 7: Total Phosphorus and Soluble Reactive Phosphorus in the Kalamas River

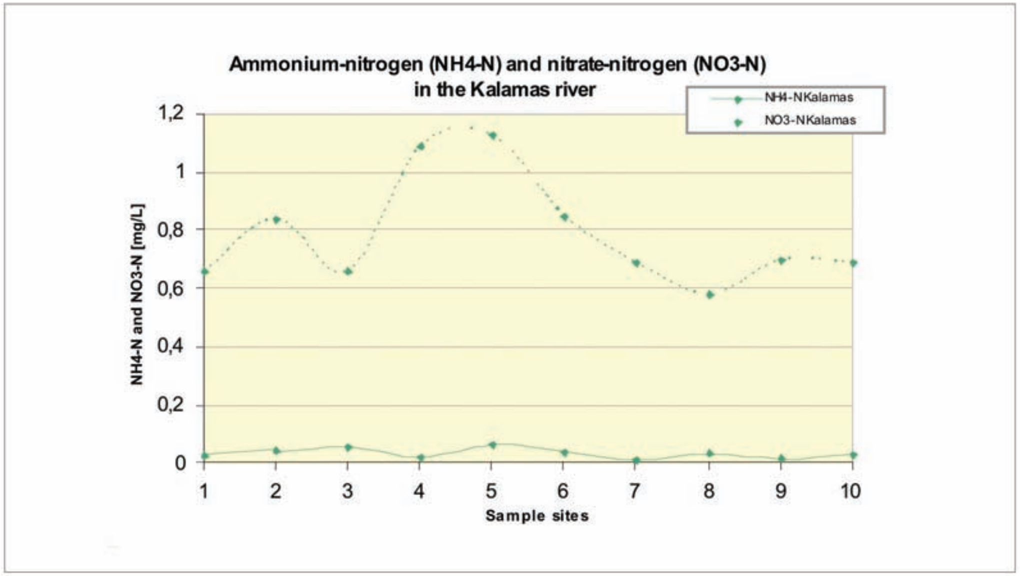

Figure 8: Ammonium-Nitrogen and Nitrate-Nitrogen in the Kalamas River

Unlike land plants, the diatoms have a special cell wall consisting of two silicate shells. These shells are extremely stable, weather resistant and exhibit specific structures whereby the individual species can be differentiated microscopically from one another (Fig. 4) .

Besides a characteristic shell, most types also exhibit an adaptation to specific ecological conditions. Depending on the level of water pollution, e.g. due to different nutrients, different diatom groups are formed.
As a result, diatoms are ideal as bio-indicators for the analysis of egological conditions.
A 'trophic index' is calculated from the relative frequencies of these types found at a specific location, which ultimately describes the water quality. To date, only a few countries have developed their own trophic indices. In Greece, the development of an appropriate indicator system on the basis of diatoms still needs to be established. According to Rott, the trophic index, that was developed for waters that flow through the limestone in Germany and Austria can be transferred to the selected area under investigation in Greece because of the similar geological conditions.

Within the diatom analyses, a total of 258 different types were determined. Physical, chemical, and the diatom-based trophic index show that, for large stretches, the Kalamas is heavily polluted with nutrients. Only the upper reaches of the Kalamas are characterised by better water quality. In addition to the treated wastewater from Ioannina, agricultural practices adjacent to the river contribute significant pollution. The EU Water Framework Directive demands that a 'good' ecological condition is achieved in all surface waters before 2015. Urgent changes to the Kalamas river are required in order to achieve this goal. Not only does the water quality need to be improved but it is also essential that environmental awareness be promoted within the population.