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Is the Iron Gate I reservoir on the Danube River a sink for dissolved silica?

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Abstract. Damming rivers changes sediment and nutrient cycles downstream of a dam in many direct and indirect ways. The Iron Gates I reservoir on the Yugoslavian-Romanian border is the largest impoundment by volume on the Danube River holding 3.2 billion m^3 of water. Silica retention within the reservoir in the form of diatom frustules was postulated to be as high as 600 kt $year^{-1}$ in previous studies using indirect methods. This amount of dissolved silicate was not delivered to the coastal Black Sea, and presumably caused a shift in the phytoplankton community there, and subsequent drastic decline in fishery. We directly quantified the amount of dissolved silicate (DSi) entering and leaving the reservoir for 11 continuous months. The budget based on these data reveals two important facts: (1) only about 4% of incoming DSi was retained in the reservoir; (2) the DSi concentrations were relatively low in the rivers upstream of the reservoir compared to regional and global averages. Thus damming the Danube at the Iron Gates could not have caused the decline in DSi concentrations documented downstream of the impoundment. Rather, this change in DSi must have occurred in the headwaters of the Danube River. Potential reasons include the construction of many dams upstream of the Iron Gates, hydrologic changes resulting in lower groundwater levels, and clogging of the riverbed limiting groundwater–river exchange.

Introduction

When rivers are dammed, the slowdown of the flow intensifies particle settling, turbidity decreases and light transmissivity increases, enhancing *in situ* primary production. After algal blooms the phytoplankton settles to the bottom of the reservoir with the siliceous frustules of diatoms sinking faster than other algae. Slow dissolution limits the diffusion of dissolved silicate (DSi) back into the water column, resulting in an overall export of silicate to the sediment. Other nutrients, such as phosphorus (P) and nitrogen (N) undergo the same process; however, they are recycled more intensely than silica (Billen et al. 1991). At least part of the organically bound nutrients is released rapidly within the water column or shortly after sedimentation. Therefore the Si/N and Si/P ratios of the water in the outlet of the reservoir might change. The nutrient ratios are further changed as P and N removal is compensated by anthropogenic inputs along the river through agriculture, industry and urban effluents, whereas no such compensation occurs for dissolved silicate. As a consequence, the coastal seas receive a completely altered composition of nutrients. The low DSi and high P and N concentrations favor the growth of non-siliceous algae. This shift in phytoplankton composition in turn

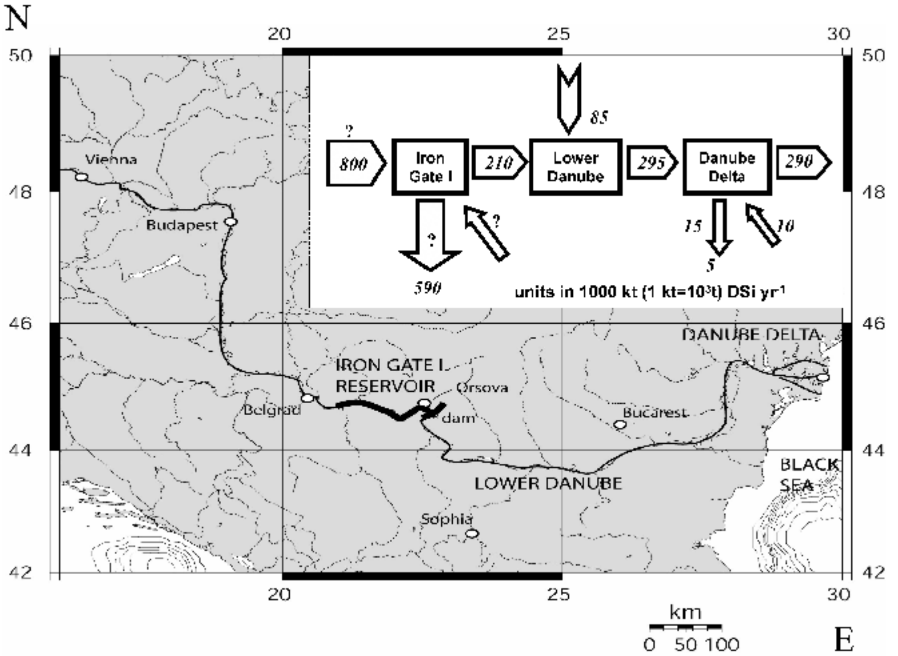

Figure 1. Map of the Danube river with Iron Gate I reservoir, the Danube Delta and the Northwest shelf of the Black Sea. Insert: Mass balance for dissolved silicate (DSi) for the lower Danube system. Fluxes in 10^3 metric tons of DSi are based entirely on information from different literature sources (see text).

affects the whole food web (Turner et al. 1998; Humborg et al. 2000). Losses of Si in man-made lakes have resulted in declines of dissolved silicate in many river waters after dam closure (Mayer and Gloss 1980; vanBennekom and Salomons 1981; Wahby and Bishara 1982; Conley et al. 1993; Conley et al. 2000). Another mechanism for decreasing Si in rivers due to damming was postulated recently by Humborg et al. (2002). In a case study of headwaters in Sweden these authors found evidence for decreasing weathering rates and lower Si-export in catchments with reservoirs.

Measurements in the coastal waters of the Northwestern Black Sea revealed that DSi declined since 1975, exactly after the largest impoundment on the major tributary, the Iron Gate dam I on the Danube River, was completed. Humborg et al. (1997) postulated that the "missing" silica in the coastal Black Sea was trapped in the Iron Gate reservoir. They estimated that around 600 kilotons (kt) Si year^{-1} was lost to the sediments of the reservoir (Figure 1). The Iron Gates dam has also been postulated to retain phosphorus and to a lesser extent nitrogen (Perisic et al. 1991; Gils 1999). A more precise nutrient mass balance of the Iron Gates is therefore of considerable interest, in order to test these different nutrient sink hypotheses. In this study, we first present a mass balance for dissolved silicate based on published data. This mass balance supports the hypothesis that dissolved silicate is efficiently retained in the Iron Gate I reservoir. The proposed hypothesis is then compared with results of a monitoring program over 11 continuous months. Inflow to the reservoir and outflow were sampled weekly during 2001 with the goal of quantifying directly the retention of dissolved silicate in the Iron Gate reservoir. More detailed accounts on the phosphorous and nitrogen budgets will be given elsewhere.

Study site

The catchment of the Danube River belongs to 14 different countries. It is the largest tributary to the Northwestern Black Sea. The Iron Gate I is the largest single hydropower dam and reservoir system along the entire Danube River (the next upstream and the second largest is Gabcikovo). The Iron Gate I reservoir marks the border between Romania and Yugoslavia and is jointly operated by the two countries. At the 1100 m wide Iron Gate I dam, the river shows an exceptional hydropower potential due to an average flow of $5600\,m^3\,s^{-1}$ and a dam height of 34 m. The second, smaller reservoir Iron Gate II serves for balancing the hydropeaking regime. The entire Iron Gate reservoir is 117 km long, with a total water volume of $3.2 \times 10^9\,m^3$ and 10,000 ha surface area. The volume of the individual reservoirs is 2.4×10^9 and $0.8 \times 10^9\,m^3$ for Iron Gates I and II, respectively. Based on an average discharge the water residence time in these two combined reservoirs is 6.5 days (Zilke 1999).

Method

The monitoring of the Iron Gate reservoir started in January 2001 and ended in December. Weekly samples were taken at nine monitoring stations between Bazias at km 1073 (the inflow of the reservoir) and km 937 (downstream of the dam) during this period (Figure 2). Samples were obtained from 1 m depth, and at middle and bottom of the water column using a Niskin bottle. Duplicate water samples were filtered through a 0.45 µm polycarbonate membrane immediately after sampling and kept in the 50 ml plastic bottles in a cool box until analyzed within one day. Samples were analyzed photometrically for dissolved silicate following standard procedures (Strickland and Parsons 1968). In addition, two cruises completed the monitoring program at high and low water level (March and October) with seismic measurements, coring, and water quality and turbulence measurements. Three sediment traps were installed in two major bays and about 500 m in front of the dam (Figure 2, sites C, D, F).

A mass balance with three compartments was calculated using published data of the Danube River and the Black Sea: the Iron Gate reservoirs, the lower Danube and the Danube Delta (Figure 1). Each compartment has a riverine input and output term, a total sedimentation rate, recycling within the compartment, and lateral input from the watershed. The lateral input is neglected in the Iron Gate compartment, because the catchment along the reservoir is small. Two further assumptions are

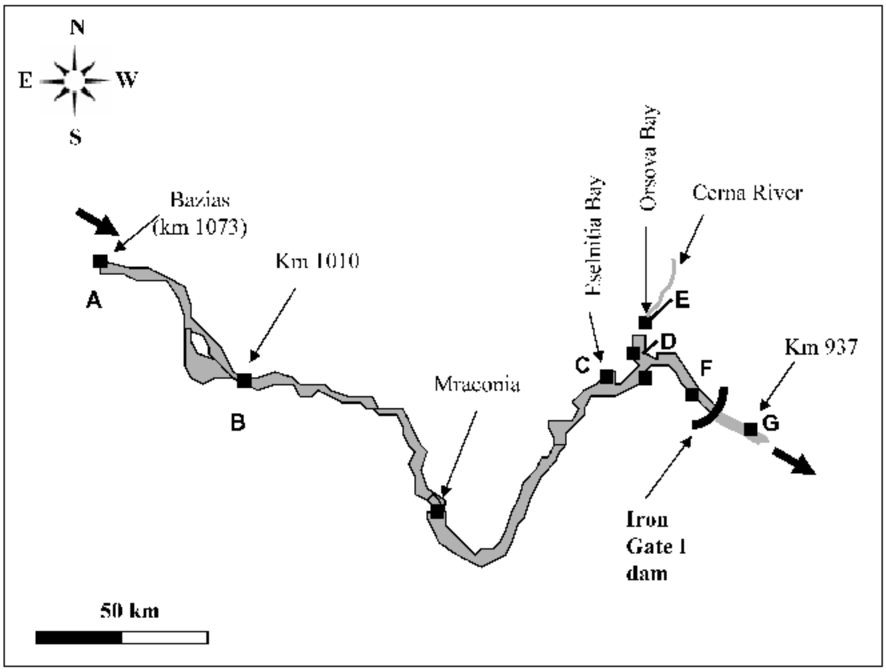

Figure 2. Map of Iron Gate 1 reservoir showing sampling sites and major tributary Cerna River.

made due to the lack of information: (1) no net-sedimentation is postulated for the compartment of the lower Danube; (2) no lateral input is considered in the Danube Delta.

Mass balance based on published data

The net-sedimentation in the Iron Gates compartment was estimated by Humborg et al. (1997 and 2000) based on measurements in the Danube Delta channels and the Black Sea. According to the authors, the load of dissolved silica (DSi) entering the Black Sea decreased by 590 kt Si year^{-1} (1 kt = 1000 metric tons) since 1975, when Iron Gate I was completed. They conclude that this amount of DSi was trapped behind the Iron Gate dams in the form of biogenic silica (BSi). A similar decrease of dissolved silicate was observed in the surface waters of the central Black Sea and was related to a reduction of input from the Danube rather than higher removal of biogenic silica by *in situ* diatom production (Ittekkot et al. 2000). An independent estimate of DSi retention can be made by using the sediment accumulation of 30,000 kt year^{-1} given by Panin et al. (1999) and the average biogenic silica concentration of 1.9% of the suspended solids measured by Reschke (1999). This calculation yields a Si retention of 569 kt Si year^{-1} in the Iron Gates.

The results of the different approaches are very similar and all support the hypothesis that a considerable amount of DSi could be transformed into biogenic silica and retained in the reservoirs. To date there were no data available for total sedimentation, recycling, input and output from the reservoirs. The latter two will be derived from balancing the budget presented here.

For the Lower Danube compartment, the only source of dissolved silicate along the river is the input from the catchment. Unlike other nutrients such as N and P, which have some of their source in anthropogenic activities, Si input depends on weathering rates only. Based on an average weathering rate of $26\,t\,km^{-2}\,year^{-1}$, and an average SiO_2 concentration of 2%, a Si weathering rate of $0.36\,t\,Si\,km^{-2}\,year^{-1}$ can be estimated (Berner and Berner 1996). Multiplying this rate with the catchment area below the Iron Gates ($240{,}000\,km^2$) yields a Si load of $85\,kt\,Si\,year^{-1}$, which is assigned as lateral input to compartment 2 (Figure 1). This value has to be considered as an upper limit because the main tributaries along this stretch of the Danube, the rivers Olt and Siret are heavily dammed. According to Word Commission of Dams (Zinke 1999), the 43 reservoirs on the river Olt have a capacity of $1.75 \times 10^9\,m^3$ water and the 88 hydropower dams on river Siret store a volume of $1.86 \times 10^9\,m^3$ water. Therefore Si retention within these reservoirs might occur and reduce the Si load. For lack of detailed information it is assumed that no significant sinks for DSi occur within the river between the reservoirs and the Danube Delta, despite some small wetlands upstream of the delta, which might act as minor sinks.

The only major sink of dissolved silicate expected below the dam are wetlands. De Master (1981) postulated that, on a global basis, about 20% of the DSi are removed in estuaries and coastal wetlands. The reed beds and the shallow lakes in the Danube Delta may act as such a nutrient trap. So far, however, only short-term data are available, which indicate strong spatial and seasonal variability: In three different Danube Delta lakes short-term retention for Si varied from 7 to 82% (Friedrich et al. 2003). However, only 10% of the Danube water enters the wetlands and lakes (Bondar 1996), with 90% of the river water flowing directly through the main channels into the Black Sea. Extrapolating the measurements of three lakes to all the delta lakes and over a whole season yields a total sedimentation of $15\,kt\,year^{-1}$. According to Friedrich et al. (2003) $10\,kt\,year^{-1}$ are recycled during the year leaving a net sedimentation of $5\,kt\,year^{-1}$ for the delta lakes.

Estimates of the Si load within the Danube River are only available at the outlet to the Black Sea (Sulina Branch). These loads are $333\,kt\,Si\,year^{-1}$ according to Humborg (1995, average for the years 1979–1992), $280\,kt\,Si\,year^{-1}$ according to Cociasu and Popa (personal communication) for 1995 and $310\,kt\,Si\,year^{-1}$ for 1997. All these output estimates are based on concentration measurements and water discharge. With approximately $290\,kt\,year^{-1}$ entering the Black Sea, $5\,kt\,year^{-1}$ retained in the delta, $85\,kt\,year^{-1}$ input from the catchment below the dam and $590\,kt\,year^{-1}$ trapped behind the dam it follows that $800\,kt\,year^{-1}$ ($290 + 5 + 590 - 85$) are brought by the Danube river into the reservoir (Figure 1). A load of $800\,kt\,year^{-1}$ at Bazias translates in mean concentration of $161\,\mu M$ DSi using an average discharge of $5600\,m^3/s$. This value is similar to the global average in river waters of 150 μM DSi (Treguer et al. 1995). The expected concentration below the dam is about four times lower (210 kt $year^{-1}$ or an average 43 μM DSi). The actual data, however, reveal some surprising facts.

Results

During 2001 DSi concentrations were measured at nine monitoring stations (Figure 2). The results of the two stations A and G, monitoring input and output, are shown in Figure 3. Input concentrations of DSi at Bazias varied between 25 and 160 μM. The lowest values occurred in May – June and August – September (25 and 32 μM DSi, respectively) when the discharge was decreasing to lower levels of 5000 and 3000 $m^3 s^{-1}$, respectively. The outflow concentrations of DSi at km 937 were similar and the overall pattern followed the results at Bazias closely. After the spring flood in April (discharge 8000 $m^3 s^{-1}$) three shorter flood events occurred during summer by end of June, beginning of August and end September with discharge peaks of about 8400, 5500 and 7300 $m^3 s^{-1}$. During these three periods DSi concentrations raised to high levels and there were slight differences of 1.5–3.4% with the output showing lower concentrations. Dissolved phosphate concentrations were also higher during these flood events, which indicates that diatom blooms in the reservoir were triggered by the increasing nutrient concentrations associated with the short periods of summer floods.

The ratio of DSi to dissolved inorganic nitrogen (DIN) is another important factor for diatom blooms. Ratios of DSi/DIN below 1.0 favor the growth of non-silicious plankton (Turner and Rabalais 1991). Values for DIN were obtained by adding the measured concentrations of nitrate, nitrite and ammonia. In Figure 4 the molar ratio DSi/DIN is plotted over time for surface samples (1 m below the surface) from Orsova Bay (Figure 2, site D), one of the major bays of the Iron Gate reservoirs. The ratios varied between 0.5 and 1.5, with high values favoring diatoms only during the spring flood and the three subsequent flood events.

Comparing the two time series, we conclude that the retention within the reservoir was negligible with the exception of the flooding periods. The systematically smaller outflow concentrations observed in mid June – mid July, the first week of August, and end September – beginning of October were probably due to primary production with formation of siliceous frustules by diatoms. Only in December the situation was reversed, more DSi was leaving the reservoir than delivered at the inflow.

The load estimates for DSi were calculated as follows: first a daily DSi concentration was calculated by interpolation between the measured values. These concentrations were then multiplied with the daily discharge measurements at Bazias and at the Iron Gate dam, respectively. This procedure was preferred to a discharge – concentration relationship because the discharge at Bazias was governed by the release of the dam. Therefore the discharge was not directly controlled by hydrological conditions such as rain events with high runoff, which influence nutrient concentrations. The DSi mass load calculated for Bazias yielded a value of

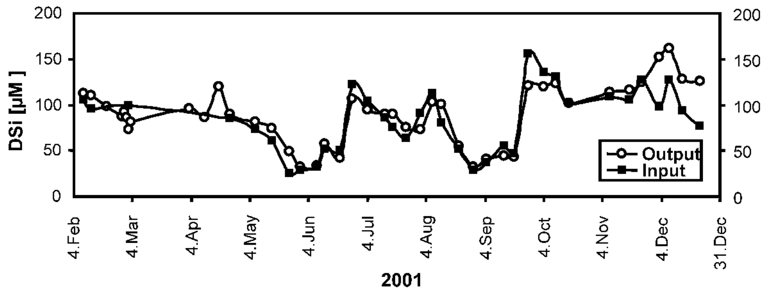

Figure 3. Time series of DSi concentrations at Bazias (input to the Iron Gate I reservoir, sampling site A) compared to time series from below the dam (output, sampling site G).

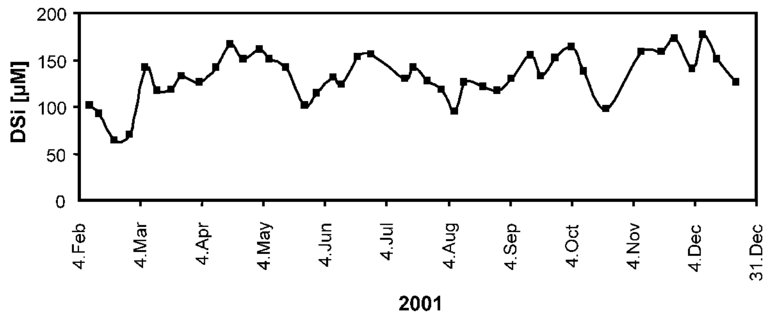

Figure 4. Time series of DSi concentrations in the tributary Cerna.

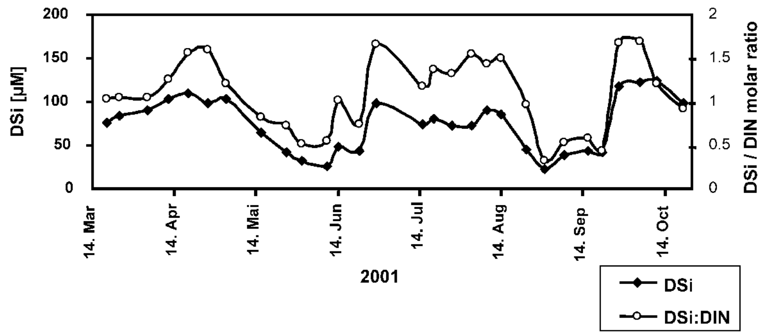

Figure 5. Variation in the DSi concentration compared to the molar ratio of DSi to dissolved inorganic nitrogen (DIN) in Orsova Bay (sampling station D).

396 kt Si for 2001. At the outflow at km 937 the mass load was 380 kt for the same year. With these values, the DSi retention of 16 kt Si year^{-1} in the reservoir was a modest 4% of the amount entering the reservoir.

The DSi concentrations of the water entering Iron Gate averaged 80 μM, which was far below the average global river concentration (150 μM, Treguer et al. 1995). Cerna River, a relatively natural tributary to the Iron Gate reservoir (Figure 2), showed 60% higher DSi concentrations than the Danube through the year. Values varied from 68 to 174 μM with a yearly average of 130 μM (Figure 5). This could imply that the Danube water reaching the Iron Gate was already depleted of dissolved silicate compared to its tributaries.

Discussion

The comparison of the concentration of DSi in the water entering and leaving the Iron Gate reservoir clearly shows that only 4% of the DSi is trapped behind the dam. The reservoir acts as a sink for 16 kt Si year^{-1}, which is substantially less than the published value of 590 kt Si year^{-1}. The arguments put forward in the literature were based on the change in DSi concentration at the mouth of the Danube River (Cociasu et al. 1996) and direct measurements of biogenic silica (BSi) on only one sediment core from the reservoir (Reschke 1999). Accurate biogenic silica (BSi) measurements in terrigenous influenced systems are often jeopardized by high clay mineral content (Ragueneau and Treguer 1994). Dissolution of clay minerals might account for the high BSi content of the Iron Gate sediment core. Apart from siliceous diatom frustules, phytolithes may account for BSi concentrations in sediments. Phytolithes are the remaining siliceous part from plants, which remain in soils and are eventually transported within the aquatic system. Conley (2002) has recently postulated their importance.

As already estimated by Reschke (1999) a biogenic Si concentration on the order of 2% of total suspended solids would be necessary to explain the decrease in DSi at Sulina, which was linked by Humborg et al. (1997) to the closing of the Iron Gates. Such a substantial fraction should be easily detectable. Three sediment traps were installed in March 2001 at sites C, D and F (Figure 2) and were sampled monthly until October 2001. However, scanning electron microscopy (SEM) performed on a representative number of samples from the traps and from sediment cores revealed that neither diatoms frustules nor phytolithes formed a substantial part of the sediment. Figure 6 shows one of the very few electron micrographs with evidence of a diatom.

Nevertheless, the time series of DSi concentration at the mouth of the Danube River and in the waters of the coastal sea show a tremendous decline after 1975 with low concentrations well documented to 1992 (Humborg et al. 1997). Our time series from 2001 indicate that diatom blooms in the reservoir were restricted to short periods of flood events. The question should therefore be addressed, whether the small DSi retention of the Iron Gates during 2001 is a recent phenomenon linked to decreasing nutrient levels in the Danube River. According to Serban and Jula (2002) no significant reduction trends were observed for the total nitrogen concentrations at the monitoring stations in Bratizlava (2.5–3 mg l^{-1}) and in Bazias (1.5–2 mg l^{-1}) between 1988 and 1998. However, the total phosphorus (TP)

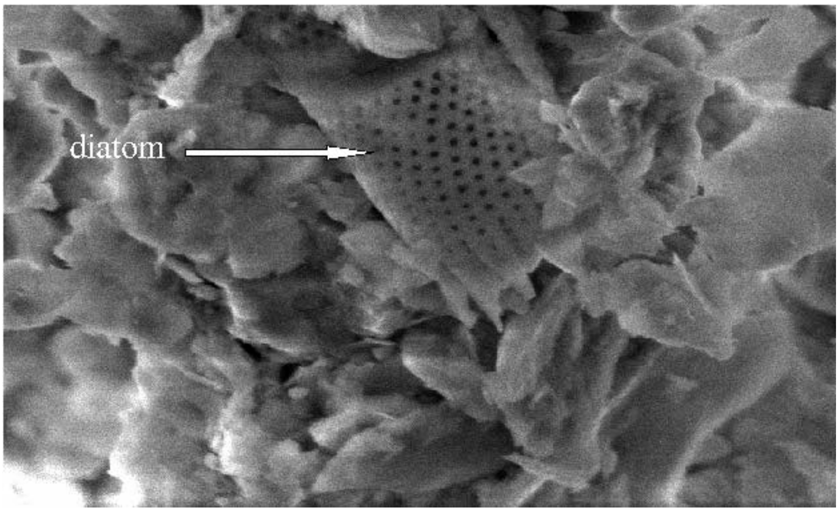

Figure 6. Scanning electron microscope photograph of sediment material from sediment trap exposed in Orsova Bay (sampling point D).

concentrations at Bratislava show a slight reduction trend from a values of $0.2\,\mathrm{mg\,l^{-1}}$ for the years 1988/89 to about $0.15\,\mathrm{mg\,l^{-1}}$ for the rest of period until 1998. At Bazias, the concentration of TP decreased more significantly after 1990 from $0.25\,\mathrm{mg\,l^{-1}}$ to an average value of $0.1\,\mathrm{mg\,l^{-1}}$ for 1992–1998. Could these lower TP concentrations be responsible for a diminished removal efficiency of the Iron Gates for DSi compared to 1975? If phosphate was the dominant factor governing the DSi removal behind the dam, then the DSi concentration at Sulina should have increased after 1989. Since this has not been observed (Humborg et al. 1997) other factors should be considered.

The concentrations measured in 2001 at the entry to the Iron Gate (80 µM on average) are well below the mean values reported from the 1960s (160 µM; Cociasu et al. 1996). Also compared with the relatively undisturbed tributary Cerna the Danube River water is depleted of DSi by about 40%. These observations imply that the governing mechanism for declining DSi concentrations in the Danube should be found upstream of the Iron Gates. Among possible mechanisms the effects of damming the headwaters and of decreasing lateral connectivity with riparian aquifers should be investigated. The many reservoirs in the headwaters of the Danube could act as sinks for DSi. Some of these reservoirs have longer residence times than the combined Iron Gate reservoirs with an average residence time of 6.5 days and could therefore be hotspots of DSi removal. However, the aquatic primary production in the headwaters may be sufficiently nutrient limited to prevent significant changes in DSi concentrations resulting from phytoplankton. For such cases the recent study by Humborg et al. (2002) revealed that even under arctic conditions with low nutrient concentrations river damming, channeling of water and reduction of water-level fluctuations resulted in smaller DSi fluxes due to decreased weathering rates. Another effect of intensive damming is the increased clogging of the river bed that may cause a considerable reduction of lateral exchange with the groundwater. Groundwater and soil water are generally rich in DSi and therefore act as an important source (Hendershot et al. 1992; Lawlor et al. 1998). Thus the input of DSi may be lowered as an indirect result of the damming by reducing the exchange with the groundwater.

Conclusion

The concentration of DSi entering the Iron Gate reservoir at Bazias is only 4% higher, on average, than in the river below the reservoir. Load estimates reveal that the retention of Si was around 16 kt for 2001, a value about an order of magnitude below what was postulated previously (Humborg et al. 1997). Although there is some growth of diatoms during flood events at sites with restricted water flow such as Orsova Bay, the effect on the overall Si load is minor. The current data indicates that DSi concentrations throughout the reservoir depend on input at Bazias and to a much lesser extent on internal process such as primary production, adsorption or redissolution.

DSi concentrations at the inflow of the Iron Gate reservoir (80 μM) were low compared to a local tributary, the Cerna River (130 μM), and the old estimates by Almazov of 140 μM for the lower Danube during 1959–60 reported by Humborg et al. (1997). Possible mechanisms are removal of DSi due to eutrophication within the whole river system or in hot spots such as reservoirs with long residence time. The decrease of lateral connectivity with riparian aquifers either due to damming or other impoundments may reduce the input of DSi to the river. These possibilities cannot be verified with the presented data and have to be addressed in a study including the headwaters and the upper river sections.

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