

## Research Article

# Biogenic silica accumulation in the sediments of Iron Gate I Reservoir on the Danube River

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**Abstract.** Damming of rivers can result in severe downstream effects such as changing sediment and nutrient fluxes that potentially affect coastal ecosystems. Closing of the Iron Gates Dams in the lower Danube River was linked to a decrease in dissolved silica flux to the Black Sea of 600,000 t yr<sup>-1</sup>. A recent study on the Iron Gate I, however, indicated a dissolved silica removal within the reservoir of only 16,000 t yr<sup>-1</sup>. Such an order of magnitude difference between actual budgets and earlier estimates is unlikely to be caused by changes in hydrological or biogeochemical conditions. In order to separate annual variations and downstream effects of damming, we analyzed the sedimentary records of biogenic silica using

dated sediments. Results confirm the detailed budgets of dissolved silica. In 2001, a total biogenic silica accumulation in the sediments of the Iron Gate I Reservoir of 19,000 t Si yr<sup>-1</sup> was determined and represents the highest retention over the past 20 years. The accumulation of biogenic silica in the Iron Gate I Reservoir was compared with data from the coastal Black Sea. Biogenic silica in the sediments of the coastal Black Sea start decreasing before Iron Gate I Dam was completed in 1971. In conclusion, construction of the largest impoundment on the Danube River, the Iron Gate I Reservoir, was not solely responsible for decreasing the silica loads downstream at the coastal Black Sea.

**Key words.** Dissolution; retention; sediment core; sediment trap; silica.

## Introduction

Rivers represent a key link between the aquatic continuum from land to ocean. Over the last century the impact of human activities on the natural regime of most rivers exceeded natural driving forces such as climate, lithology or tectonic factors (Turner et al., 1991; Messerli et al., 2000; Meybeck, 2003; Meybeck and Vörösmarty, 2005). Different impacts of dam construction on large rivers have been studied recently: the loss of biodiversity and habitats (Piz-

zuto, 2002), cumulating sediment loads in reservoirs (Vörösmarty et al., 2003; Walling and Fang, 2003), changes in thermal stratification (Preece and Jones, 2002), cold water pollution (Sherman, 2000), and disrupted biogeochemical nutrient cycles (Friedl and Wüest, 2002). Higher nutrient retention in reservoirs is generally caused by a slowdown in flow rate, promoting *in-situ* primary production. Increased *in-situ* diatom production was the principal mechanism explaining the decline of dissolved silica (DSi) observed in several dammed rivers (Mayer and Gloss, 1980; van Bennekom and Salomons, 1981; Wahby and Bishara, 1982; Conley et al., 1993; Conley et al., 2000). The biological storage of DSi in the form of diatom frustules can be analyzed as biogenic silica (BSi) in the sediment record. After algal blooms, diatoms sink

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faster than other algae. Slow dissolution limits the diffusion of Si back to the water column resulting in a net accumulation of silica in sediments. Other nutrients such as nitrogen (N) and phosphorus (P) are recycled more intensely than Si. Therefore, downstream nutrient ratios may change and cause severe problems in coastal ecosystems. Recent analyses of the acceleration of biogeochemical cycles in coastal systems demonstrate the effects of severe nutrient loading (Childs et al., 2002; Conley et al., 2002; Rabalais et al., 2002). Semi-enclosed basins such as the Black Sea (Mee, 1992; Lancelot et al., 2002) with long water residence times and low tidal energies are particularly susceptible to increased anthropogenic nutrient loads (Cloern, 2001).

Between 1970 and 2000, when high N and P loads in the Danube River were a consequence of European industrial development, increased urban population and intensive use of fertilizers in the agriculture sector, measurements at the north-western coastal Black Sea recorded a three-fold decrease in DSi concentration (Cociasu et al., 1996). This may have caused a dramatic shift in phytoplankton composition from a community dominated by diatoms to a prevalence of non-siliceous species that, in the long term, affected the entire food web (Cociasu et al., 1996; Humborg et al., 1997). The substantial Si decrease in the early 1970s was related to the construction of the largest reservoir system on the Danube, Iron Gate Reservoirs I and II. Indirect methods based on DSi changes in the Danube discharge have been interpreted as a large annual Si retention in the Iron Gates in the form of settling diatoms (BSi) of around  $600,000 \text{ t Si yr}^{-1}$  (Cociasu et al., 1996; Humborg et al., 1997) or more than 75% of the incoming load (Friedl et al., 2004). A recent mass balance in Iron Gate I Reservoir, however, resulted in a present-day (2001) DSi retention of  $16,000 \text{ t Si yr}^{-1}$ , accounting only for about 5% of the river inflow (Friedl et al., 2004; McGinnis et al., 2006). Analysis of biogenic silica in sediment cores could clarify these discrepancies. Records of BSi concentration represent a powerful tool for paleoproductivity and paleoecological reconstruction (Coleman et al., 1992; Granina et al., 1993; Qiu et al., 1993). Past trophic conditions (Carney, 1982; Dixit et al., 1992; Stoermer et al., 1985a) or historical lake phosphorus concentrations (Hall and Smol, 1992; Anderson and Rippey, 1994; Bennion et al., 1996) were reconstructed from sedimentary BSi studies. Fluctuations in the nutrient regime (Stoermer, 1978; Stoermer et al., 1985b) or changes in water residence time (Soballe and Kimmel, 1987) were quantified by investigating the diversity and abundance of diatoms over time. Only few of these paleolimnological studies have been carried out thus far on reservoir systems (Donar et al., 1996).

To re-assess the biogeochemical implications of a large dam, this paper aims at reconstructing the BSi accumulation over the last decades in the largest reservoir

on the Danube River. To clarify the published one order of magnitude discrepancies of DSi retention in the reservoir (Friedl et al., 2004; Humborg et al., 1997), the following questions were addressed: (i) what is the total BSi flux that accumulates in the sediments of the Iron Gate I Reservoir? (ii) how does the present BSi accumulation compare to the past situation during the early stages of the reservoir? (iii) and to what extent could BSi accumulation in the reservoir influenced diatom production in the coastal Black Sea?

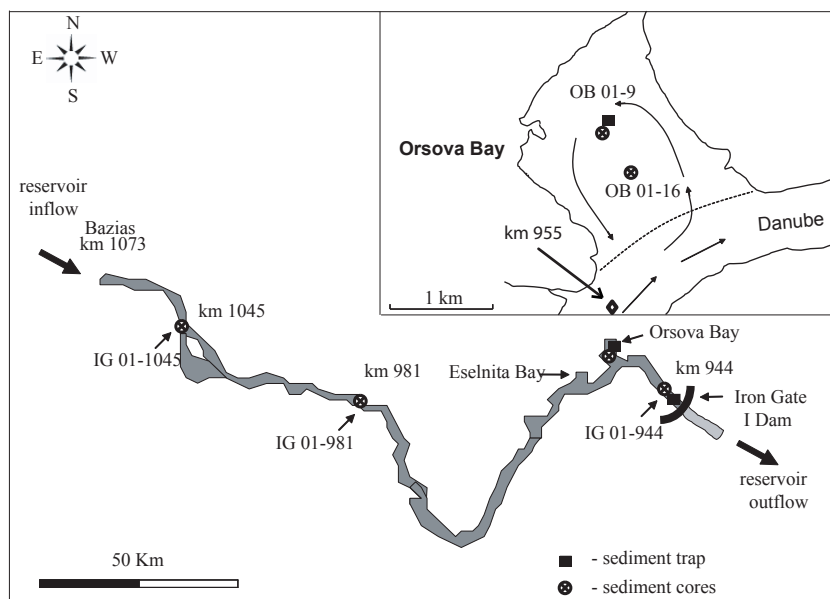
## Study site

The Danube River, the largest river in Europe after the Volga, drains approximately one-tenth of the European landmass. Starting in the Black Forest Mountains of Germany, the river flows east for 2,850 km before discharging into the north-western Black Sea through the three branches of its delta (Fig. 1). A high density of dams is found on the Upper Danube (the upper 1,000 km), averaging one dam per 17 km (Zinke, 1999). Among the high number of impoundments, the Iron Gates is the largest hydropower-dam system on the entire Danube. Located on the Lower Danube on the border between Romania, and Serbia and Montenegro (former Yugoslavia, Fig. 1), the hydropower scheme consists of two dams: upper Iron Gate I, a 1,278 m wide overflow concrete dam with 14 spillways constructed in 1971 at river km 942.4 from the Black Sea, and Iron Gate II, a similar 1,003 m wide dam completed in 1984 at river km 864 (Teodoru and Wehrli, 2005). The two reservoirs extend over 205 km with a surface area of  $156 \text{ km}^2$  and maximum volume of  $2.7 \text{ km}^3$  (Teodoru and Wehrli, 2005). The channel has a general trapezoidal shape, a mean depth of 25 (maximum depth 53) and an average width of 1,040 m. With an area of  $104.5 \text{ km}^2$  and storage capacity of  $2.1 \text{ km}^3$ , Iron Gate I Reservoir is of main importance, whereas the smaller downstream reservoir (Iron Gate II) serves mostly for mitigating peak operations.

To investigate the reservoir's role as a sediment and nutrient sink, a monitoring program was carried out between 1 February and 20 October 2001 that focussed on Iron Gate I Reservoir. Physical parameters, water chemistry, sediment and nutrient retention during 2001 are described in Friedl et al. (2004), Teodoru and Wehrli (2005) and McGinnis et al. (2006). To provide a detailed spatial and temporal overview of the sedimentary BSi accumulation, several gravity cores (Kelts et al., 1986) were taken during March 2001 near the reservoir inlet (IG 01-1045 and IG01-981) and outlet at about 2 km upstream of Iron Gate I Dam where the sedimentation of fine material is maximal (IG 01-944) (Fig. 2). Side bays were identified as main areas supporting primary production (McGinnis et al., 2006). Located on the Romanian side about 12 km upstream of the dam, Orsova Bay is the main bay within



**Figure 1.** The Danube River basin with the location of the Iron Gates Reservoir and coring locations at the Danube Delta.



**Figure 2.** Map of Iron Gate I Reservoir from the inflow at Bazias to the outflow of the dam indicating positions of cores and sediment traps.

the reservoir. Two sediment cores were taken from Orsova Bay (OB 01-9 and OB 01-16) and a sediment trap was installed in a floating position at 6-m depth (about 3 m above the bottom). A second trap was fixed on the dam lock about 0.5 km upstream of the dam wall at 5 m above the bottom (maximum water depth 31 m). Accumulated sediment in the traps was collected monthly until October 2001.

This sampling in 2001 in Iron Gate I was complemented with a coring campaign in June 2004 at the Danube Delta and coastal Black Sea to detect changes in

sedimentary BSi before and after closing the Iron Gate Dams. The sampling strategy here was based on the general north-south wind-driven water circulation along the Romanian coast (Cociasu et al., 1996) and the partition of the Danube load through the three arms of the Danube Delta (Fig. 1): the Chilia Branch to the north carries more than 60% of the Danube load, whereas Sulina in the middle and St. Gheorghe to the south share the remaining 40% (Gastescu and Oltean, 1997). Located about 5 km upstream of the Sulina Branch at a water depth of 15 m, core SL 04-3 is directly influenced by the Sulina dis-

**Table 1.** Average BSi concentration in sediment cores and sediment traps from Iron Gate I Reservoir and the coastal Black Sea.

Location		Coordinates		BSi
		N	E	[mg Si g <sup>-1</sup> ]
<b>I. Bazias – Orsova</b>				<b>2.1</b>
km 1045 (IG 01-1045)	sediment core	44°41'03"	21°40'06"	1.8
km 981 (20) (IG 01-981)	sediment core	44°31'59"	22°12'55"	2.4
<b>II. Orsova Bay</b>				<b>5.6</b>
Orsova Bay (9 m) (OB 01-9)	sediment core	44°43'30"	22°24'34"	5.3
Orsova Bay (16 m) (OB 01-16)	sediment core	44°42'40"	21°25'03"	5.7
<i>Orsova Bay – 4 months</i>	<i>sediment trap</i>	<i>44°43'33"</i>	<i>22°24'30"</i>	<i>14.1</i>
<b>III. Orsova – Iron Gate I Dam</b>				<b>7.6</b>
km 944 (IG 01-944)	sediment core	44°41'11"	22°30'54"	7.6
<i>km 943 – 7 months</i>	<i>sediment trap</i>	<i>44°41'00"</i>	<i>22°30'13"</i>	<i>6.5</i>
<b>Black Sea</b>				
Musura Bay (MB 04-5)	sediment core	45°10'46"	29°42'24"	3.6
Sulina front (SL 04-3)	sediment core	45°06'40"	29°46'49"	4.7

charge and the drifting load of the Chilia Branch. Musura Bay is situated north of Sulina City, between the Chilia and Sulina branches. With a maximum depth of 5 m, it represents an area influenced indirectly by the particulate river load. Core MB 04-5 was obtained from the middle of Musura Bay at a water depth of 1.7 m (Fig. 1). Core locations are documented in Table 1.

## Methods

Spatial distribution and accumulation of sedimentary BSi in Iron Gate I can be calculated from the concentration profiles in dated sediment cores. Sediment traps show the seasonality in the settling BSi flux. By comparing the results in the reservoir with those from the coastal Black Sea, the influence of closing the dam on downstream silica fluxes can be evaluated. All cores were transported in an up-right position and stored in the cool room at 4°C until opened in the laboratory. Cores were cut into half for description, photographed, and sub-sampled at 1-cm increments. Wet sub-samples were freeze-dried for 3 days and the measured water content was used for porosity determinations. Samples were analyzed as follows:

### Dating

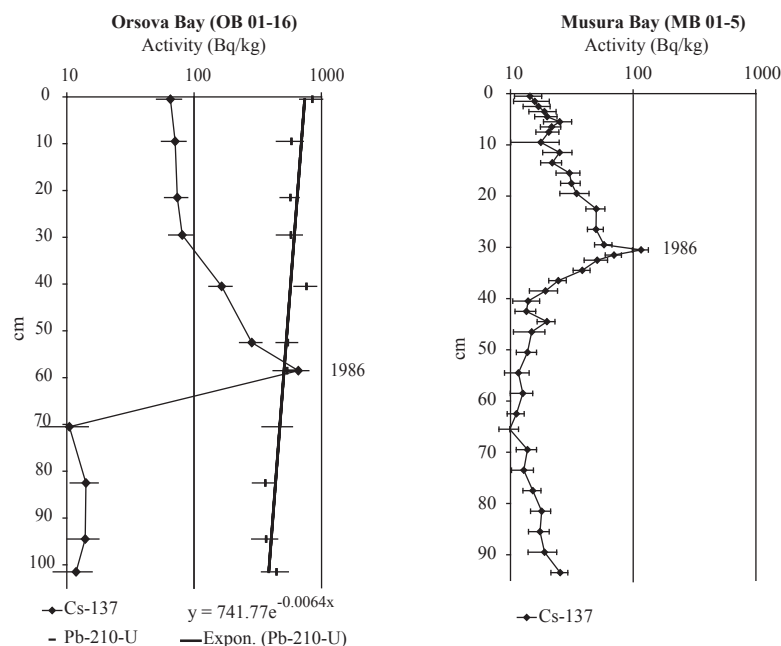
Expecting high sedimentation rates, the longest cores of Iron Gate I Reservoir (OB 01-16 and IG 01-944) and the Black Sea (SL 04-3 and MB 04-5) were used for dating.

Freeze-dried samples from each cm interval were analysed for sediment chronology using the <sup>210</sup>Pb method of Goldberg (1963) and Krishnaswami et al. (1971) and the artificial <sup>137</sup>Cs radionuclide (Pennington et al., 1973). Precision of the measurements was 3%. Sedimentation rates (cm yr<sup>-1</sup>) were corrected for compaction according to Appleby and Oldfield (1978) and Robbins (1978), and a maximum error of 5% was considered.

### Biogenic silica

In general, silica components in sediment samples can be partitioned among diatoms, sponge spicules, and silicate minerals (Conley et al., 1993). Distinguishing the source of BSi is possible due to different dissolution rates of these silica components. Labile diatom frustules are completely dissolved within the first 2 h of digestion. Sponge spicules of larger size need longer to dissolve completely, whereas silicate minerals have the slowest dissolution rates (DeMaster, 1981).

The single-step wet-alkaline leach method developed by Mortlock and Froelich (1989) and outlined earlier by Eggiman et al. (1980) was applied for BSi determination. About 30-mg freeze-dried material from each sediment core and sediment trap was transferred to a Teflon crucible and treated with 10-ml 1M NaOH. After digestion for 3 h at 90°C in an oven, the centrifuged aliquot was treated with 0.075M HNO<sub>3</sub> and BSi was measured within 24 h by inductively-coupled plasma, optical-emission spectroscopy (ICP-OES/Spectro-Ciros). Based on simultane-



**Figure 3.** Sediment core dating from Orsova Bay and the coastal Black Sea showing the profiles of radionuclides  $^{137}\text{Cs}$  and  $^{210}\text{Pb}$ . The Cs peak represents the Chernobyl accident in 1986.

ous determination of aluminum and sodium, the ICP technique allows for the correction of Si derived from dissolution of silicate minerals (Eggiman et al., 1980). All concentrations referred in this paper as BSi represent elemental Si ( $\text{mg g}^{-1}$ ) attributed to diatom dissolution. The precision of the method was 10%.

## Results

### Rates of sedimentation

Even with lengths of 38 and 65 cm, respectively, cores upstream of the dam (IG 01-944) and at the Sulina discharge (SL 04-3) did not include the most recent  $^{137}\text{Cs}$  peak of the Chernobyl accident in 1986. Also, due to particle remobilisation leading to a dilution effect in these high sedimentary zones,  $^{210}\text{Pb}$  activity in both cores was generally low and showed no clear trend.

Using the  $^{210}\text{Pb}$  method and supported by the inventory of artificial  $^{137}\text{Cs}$  radionuclide, the middle core of Orsova Bay (OB 01-16) indicated a sedimentation rate of  $4.9 \text{ cm yr}^{-1}$  (Fig. 3). A similar sedimentation rate of  $5 \text{ cm yr}^{-1}$  was calculated by Reschke (1999) for the second largest bay of the reservoir, Eselnita Bay. With upper sediment characterised by porosity and density values of 85% and  $2.5 \text{ g cm}^{-3}$ , respectively, recent sediment flux for Orsova Bay was calculated at  $50.3 \text{ g m}^{-2} \text{ day}^{-1}$  (Table 2). A 2-m long sediment core from river km 947.2 (about 4 km upstream of the dam) was used by Reschke (1999) to estimate a sedimentation rate of  $23.3 \text{ cm yr}^{-1}$  or a sediment

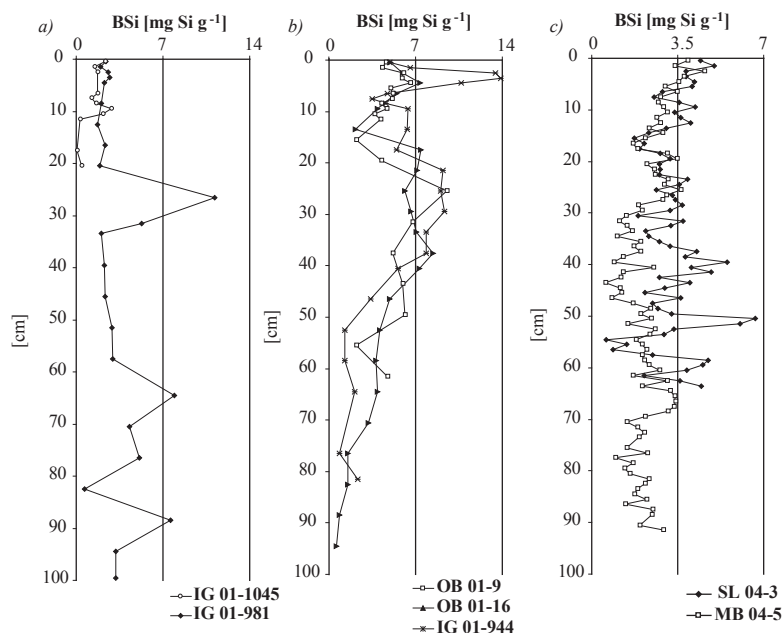
flux of  $239.4 \text{ g m}^{-2} \text{ day}^{-1}$ . More information on sedimentation rates in Iron Gate I reservoir derived from sediment cores and total suspended solids (TSS) mass balance is given in Teodoru and Wehrli (2005).

At the Black Sea, the Musura Bay core (MB 01-5) included the  $^{137}\text{Cs}$  peak of the Chernobyl accident at a depth of  $\sim 30 \text{ cm}$ , suggesting a sedimentation rate of  $1.7 \text{ cm yr}^{-1}$  (Fig. 3). Unfortunately, due to low activity and unclear gradient, the sedimentation rate was not confirmed by  $^{210}\text{Pb}$  analysis. Gulin et al. (2002) measured a sedimentation rate of  $1.15 \text{ cm yr}^{-1}$  from a nearby core on the Black Sea shelf, in front of the Danube discharge at a water depth of 26 m. Based on literature values, an average of  $1 \text{ cm yr}^{-1}$  was estimated by Teodoru et al. (accepted) for the river influenced area of the north-western shelf of the Black Sea. Accordingly, a sedimentation rate of  $1.7 \text{ cm yr}^{-1}$  was considered representative for Musura Bay and used in further calculations.

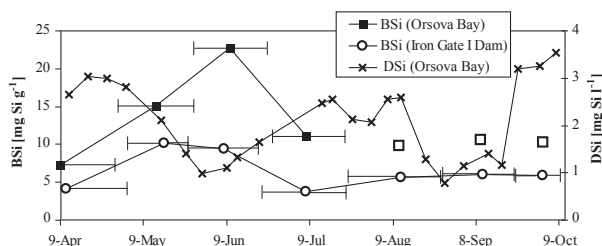
### BSi in sediment cores

Core profiles of BSi concentrations in Iron Gate I Reservoir are plotted with results of the Black Sea sediments (Fig. 4). The upstream cores of the reservoir (IG 01-1045 and IG 01-981) showed a constant concentration of about  $2.3 \text{ mg Si g}^{-1}$  for the upper 10 cm. With increasing depth, the concentration approached zero in core IG 01-1045 but increased to almost  $11 \text{ mg Si g}^{-1}$  at  $\sim 26 \text{ cm}$  in IG 01-981 (Fig. 4a). A significant correlation was found between the two cores of Orsova Bay (OB 01-9 and OB





**Figure 4.** Down-core Si concentration profiles of Iron Gate I Reservoir (a and b) and the Black Sea sediments (c).



**Figure 5.** Seasonality of biogenic silica (BSi) concentration measured in the sediment trap at Orsova Bay and Iron Gate I Dam together with time series dissolved silica (DSi) concentration in Orsova Bay. BSi values from July to October in Orsova Bay (empty squares) were approximated from the BSi pattern at the dam site.

01-16) and core IG 01-944 upstream of the dam (Fig. 4b). From bottom to top, a general pattern of increasing concentration was identified with low values of around  $2 \text{ mg Si g}^{-1}$  to an average of  $5.5 \text{ mg Si g}^{-1}$  in Orsova Bay (OB 01-9 and OB 01-16) and  $8 \text{ mg Si g}^{-1}$  upstream of the dam (Table 1). Values from sediment traps were added in Table 1 only for comparison and were not considered when calculating the average concentration of each sedimentary area.

Profiles of BSi concentration measured in two sediment cores of the coastal Black Sea were well correlated (Fig. 4c). Large fluctuations in BSi concentration measured in front of the Sulina branch in core SL 04-3 indicates variations in Danube discharge (Humborg et al., 1997) as well as large oscillations in transported BSi load from upstream areas, especially from the Danube Delta. The Musura Bay

core (MG 04-5), under indirect influence of the particulate load, showed three distinct patterns (Fig. 4c). From bottom to top: (a) a constant concentration of about  $1.9 \text{ mg Si g}^{-1}$  between  $-90$  to  $-70 \text{ cm}$ ; (b) a sharp increase to around  $3.5 \text{ mg Si g}^{-1}$  at  $-68 \text{ cm}$  followed by a continuous decrease to  $0.9 \text{ mg Si g}^{-1}$  until  $-44 \text{ cm}$ ; and (c) a graduate increase over the last  $44 \text{ cm}$  to  $4.2 \text{ mg Si g}^{-1}$ .

### BSi in sediment trap

Time series BSi concentration from sediment traps deployed in Orsova Bay and at the dam showed a constant increase from April to June from  $7.3$  to  $22.8 \text{ mg Si g}^{-1}$  at Orsova Bay and from  $4.1$  to  $9.4 \text{ mg Si g}^{-1}$  at the dam (Fig. 5). Both sediment traps showed a decrease in BSi concentration from June to July. An approximately constant value of around  $6 \text{ mg Si g}^{-1}$  was measured in the sediment trap at the dam between July and October, whereas, no data were available for Orsova Bay (due to the loss of equipment after July).

## Discussion

### Sedimentary BSi accumulation

The sediment balance of total suspended solids (TSS) for 2001 (Teodoru and Wehrli, 2005) identified three sedimentary regions within Iron Gate I: a first upper stretch from Bazias to km 955 ( $300 \text{ m}$  upstream of Orsova Bay) represents  $87\%$  of the entire area with a TSS flux of  $101 \text{ g m}^{-2} \text{ day}^{-1}$ ; a second section, Orsova Bay, accounts for

**Table 2.** Three sedimentary areas within Iron Gate I Reservoir with the bulk sediment fluxes, BSi concentrations, silica fluxes and total sedimentary Si accumulation.

Sedimentary zones			Area	Accum. rate	Sediment flux	BSi concentration	BSi flux	BSi retention
			[km <sup>2</sup> ]	[cm yr <sup>-1</sup> ]	[g m <sup>-2</sup> day <sup>-1</sup> ]	[mg Si g <sup>-1</sup> ]	[g Si m <sup>-2</sup> day <sup>-1</sup> ]	[kt Si yr <sup>-1</sup> ]
<b>Iron Gate I reservoir</b>			<b>104.5</b>					<b>19.0</b>
I	Bazias - Orsova	TSS	91	9.8 <sup>(a)</sup>	100.8	2.1	0.2	7.0
II	Orsova Bay	TSS	4.5	9.8 <sup>(a)</sup>	100.5	5.6	0.6	0.9
		core	4.5	4.9 <sup>(b)</sup>	50.3		–	–
III	Orsova – Iron Gate I Dam	TSS	9	43.4 <sup>(a)</sup>	446.0	7.6	3.4	11.1
		core	9	23.3 <sup>(b)</sup>	239.4		–	–

(a) calculated from total suspended solids.

(b) calculated from sediment core.

4.5% of the total area with a comparable sedimentary flux of 100 g m<sup>-2</sup> day<sup>-1</sup>; and a third lower stretch from Orsova Bay to Iron Gate I Dam that includes 8.5% of the reservoir area and the highest flux of 446 g m<sup>-2</sup> day<sup>-1</sup> (Table 2). Compared to fluxes calculated from sediment cores, the TSS values were systematically higher by a factor of two. Sediment cores reflected a local value integrated over a few decades, whereas the TSS estimates were subject to temporal fluctuations but integrated over large areas. Therefore, TSS fluxes were used in further calculations (Teodoru and Wehrli, 2005).

From the topmost 10 cm of each core within the reservoir, average concentrations were calculated to represent the recent sedimentary BSi accumulation (Table 1). Average values of 2.1 mg Si g<sup>-1</sup>, 5.6 mg Si g<sup>-1</sup> and 7.6 mg Si g<sup>-1</sup> were estimated for each sedimentary zone. Multiplying the concentrations by respective TSS fluxes, Si fluxes to sediment were quantified (Table 2). Scaling the data by the area of the specific zone and summing the results, the total sedimentary Si accumulation in Iron Gate I was calculated at 19 ± 2 kt Si yr<sup>-1</sup> (1 kt = 10<sup>3</sup> metric tons). A previous study by Friedl et al. (2004) based on a DSi mass balance for the same year (2001) quantified DSi retention within the reservoir at 16 ± 2 kt Si yr<sup>-1</sup>. The two independent estimates are in excellent agreement. Two questions remain open: (i) what rates of *in-situ* primary production are required to annually transform 16 kt DSi into BSi? and (ii) where does the primary production mainly take place as the main channel of the reservoir is too turbulent and turbid to support high rates of primary production (McGinnis et al., 2006)?

### BSi dissolution

BSi dissolution in reservoirs is generally a slow process and depends on many factors such as thermodynamic driving forces, accumulation rate of bulk material, and the

BSi flux itself (Broecker and Peng, 1982; McManus et al., 1995; Van Cappellen and Qiu, 1997a, b; Kohly, 1998; Gallinari et al., 2002). In deep water bodies such as Lake Baikal or in ocean basins, a broad range of sinking rates of 7–100 m d<sup>-1</sup> determines the fraction of BSi dissolved in the water column. In Lake Baikal only 0.1 to 9% of the diatoms produced in the surface water reach the lake floor (Ryves et al., 2003). For the shallow Orsova Bay with a mean depth of 10 m, the theoretical residence time of diatom particles in the water column is comparatively short (0.1 to 1.5 days) and can therefore be neglected.

Measurements at the sediment-water interface in the North Atlantic and equatorial Pacific have shown that the time required for dissolution to half of the initial BSi concentration was between 300 to 14,300 years (Gallinari et al., 2002). At four orders of magnitude higher bulk accumulation rates, the dissolution at the sediment-water interface in Iron Gate I will be limited by extremely short exposure times before burial. A strong correlation between BSi flux and the percentage dissolution was determined by Gallinari et al. (2002), where accumulation fluxes higher than 0.006 g Si m<sup>-2</sup> day<sup>-1</sup> resulted in dissolution of <20%. As BSi fluxes in the reservoir were two to three orders of magnitude higher (0.7 to 3 mg Si m<sup>-2</sup> day<sup>-1</sup>), the estimated percentage of dissolved BSi was negligible. Therefore, concentrations measured in sediment cores of the Iron Gates are valid indicators for the BSi concentration of suspended particles in the water column at specific sites.

### Seasonality of diatom settling

Sediment traps can offer important information on the seasonality of diatom blooms. Installed in a floating position at 6 m water depth and about 3 m above the bottom, BSi concentrations measured in the Orsova Bay sediment trap was considered to represent the settling rate from *in-*

**Table 3.** Seasonality of BSi in the sediment trap at Orsova Bay. Values from March until July are based on direct measurements, whereas the *italics* values (from July to October) represent extrapolated concentrations using the pattern of sedimentation rates at the dam. Underlined values between October and March were assumed to be lower than the spring concentration and were assigned a constant value of 6 mg g<sup>-1</sup>.

Sampling interval	Orsova Bay trap Si conc.	Si flux ( <i>in-situ</i> production)	Si load ( <i>in-situ</i> production)	Equivalent Primary Production
	[mg Si g <sup>-1</sup> ]	[g Si m <sup>-2</sup> yr <sup>-1</sup> ]	[kt Si yr <sup>-1</sup> ]	[g C m <sup>-2</sup> yr <sup>-1</sup> ]
March–April	7.3	268	1.2	758
April–May	15.0	550	2.5	1560
May–June	22.8	836	3.8	2370
June–July	11.2	411	1.8	1160
<i>July–August</i>	<i>10.1</i>	<i>370</i>	<i>1.7</i>	<i>1050</i>
<i>August–September</i>	<i>10.6</i>	<i>390</i>	<i>1.8</i>	<i>1100</i>
<i>September–October</i>	<i>10.5</i>	<i>387</i>	<i>1.7</i>	<i>1100</i>
<u><i>October–November</i></u>	<u><i>6.0</i></u>	<u><i>220</i></u>	<u><i>1.0</i></u>	<u><i>623</i></u>
<u><i>November–December</i></u>	<u><i>6.0</i></u>	<u><i>220</i></u>	<u><i>1.0</i></u>	<u><i>623</i></u>
<u><i>December–January</i></u>	<u><i>6.0</i></u>	<u><i>220</i></u>	<u><i>1.0</i></u>	<u><i>623</i></u>
<u><i>January–February</i></u>	<u><i>6.0</i></u>	<u><i>220</i></u>	<u><i>1.0</i></u>	<u><i>623</i></u>
<u><i>February–March</i></u>	<u><i>6.0</i></u>	<u><i>220</i></u>	<u><i>1.0</i></u>	<u><i>623</i></u>
<b>Annual average</b>	<b>9.8</b>	<b>359</b>	<b>1.6</b>	<b>1020</b>

*situ* diatom production. The colder and denser main stream water entered the bay along the bottom and therefore contributed only marginally to BSi flux in the trap (McGinnis et al., 2006).

Deployed in March 2001, the Orsova Bay sediment trap monitored the spring bloom. Unfortunately, due to the loss of equipment after July, fluxes in late summer, autumn and winter could not be calculated. Considering the close relationship between trap at the dam site and at Orsova Bay, we assumed that BSi concentration in Orsova Bay also reached a steady value of around 10 mg Si g<sup>-1</sup> after July (Fig. 5, empty squares). In extrapolating these values to calculate annual production, we were aware that data from the low productivity season are missing. The following estimate assumed that settling rates in winter (October to March) were lower than in April, representing a relatively constant rate of 220 g Si m<sup>-2</sup> yr<sup>-1</sup> (Table 3, *italics*). The annual settling rate of 360 g Si m<sup>-2</sup> yr<sup>-1</sup>, may still represent an upper estimate.

Time series of DSi concentration in Orsova Bay (Fig. 5) showed a decrease from 3 mg Si l<sup>-1</sup> in April to about 1 mg Si l<sup>-1</sup> in June. This period corresponds to the spring diatom bloom. The concentration increased at the end of the season to an almost steady value of 2.5 mg Si l<sup>-1</sup> followed by a second decrease to around 1 mg Si l<sup>-1</sup> until September. Similar to the DSi decrease in spring, this second minimum may indicate a summer diatom bloom but could also imply Si depletion in the upstream reservoirs. The average flow velocity of about 0.36 m s<sup>-1</sup> trans-

lates into a travel time of two months, and matches perfectly the observed minimum DSi concentration between August and September.

### Primary production

The average settling rate calculated from the sediment trap of Orsova Bay of 360 g Si m<sup>-2</sup> yr<sup>-1</sup> results in an annual load of 1.6 kt Si yr<sup>-1</sup>. Considering a Si/N molar ratio of 1 in nutrient replete diatoms and then converting to diatom carbon assimilation using a Redfield C/Si molar ratio of 106:16 (Redfield et al., 1963), the Si flux due to *in-situ* diatom production in Orsova Bay represents 1020 g C m<sup>-2</sup> yr<sup>-1</sup> (Table 3, *italics*). Compared to oligotrophic open oceans (50 g C m<sup>-2</sup> yr<sup>-1</sup>) or temperate lakes such as Lake Superior, Erie or Malawi (55, 160, 210 g C m<sup>-2</sup> yr<sup>-1</sup>, respectively, Guildford et al., 2003), the annual diatom production of Orsova Bay was an order of magnitude higher but comparable to coastal estuaries (1,200 g C m<sup>-2</sup> yr<sup>-1</sup>) and much lower than the tropical, highly eutrophic Lake Victoria at 4,000 g C m<sup>-2</sup> yr<sup>-1</sup> (Guildford et al., 2003). The value is also in the broad range of primary production in the Danube River estuary of between 80 and 1,600 g C m<sup>-2</sup> yr<sup>-1</sup> (Humborg, 1997).

High particle loads in the main channel and the preferential accumulation upstream of the dam (Table 2) suggest that Si concentrations measured in the sediment trap at the dam (Fig. 5) do not represent a realistic dataset for evaluating *in-situ* diatom production. The average Si flux



in the main channel due to *in-situ* diatom production was therefore estimated using the following approach: at  $1.6 \text{ kt Si yr}^{-1}$ , Orsova Bay contributed 10% to the total biogenic silica production of  $16 \text{ kt Si yr}^{-1}$  (Freidl et al., 2004). This translates into an in-stream diatom production of  $144 \text{ g Si m}^{-2} \text{ yr}^{-1}$  with a photosynthesis rate of  $407 \text{ g C m}^{-2} \text{ yr}^{-1}$ . Similar fluxes between 100 to  $650 \text{ g Si m}^{-2} \text{ day}^{-1}$  were estimated from sediment of Lake St. Croix on the Mississippi River (Triplett et al., 2003) and translates to an equivalent diatom production of 156 to  $865 \text{ g C m}^{-2} \text{ yr}^{-1}$ . Also, a study on a large number of Swiss lakes indicated comparable production rates from 193 to  $492 \text{ g C m}^{-2} \text{ yr}^{-1}$  (Wehrli and Wüest, 1996). At  $359 \text{ g Si m}^{-2} \text{ yr}^{-1}$ , the average flux of Orsova Bay due to *in-situ* diatom production was found to be 3× higher than the main stream flux of  $144 \text{ g Si m}^{-2} \text{ yr}^{-1}$ . This value is consistent with the general three-fold higher chlorophyll a concentrations in Orsova Bay compared to the main stream as documented by McGinnis et al. (2006).

### BSi mass balance for Iron Gate I Reservoir

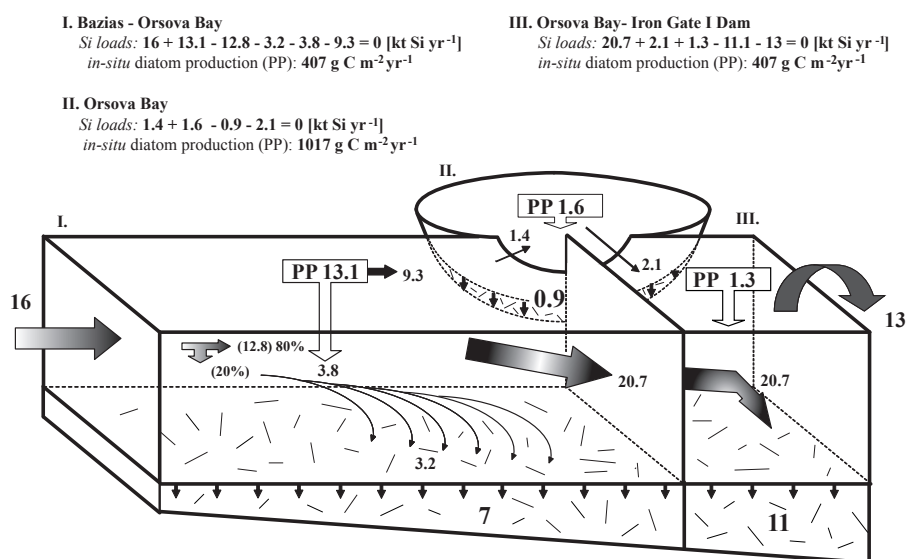
To calculate the Si balance, the reservoir was separated into three compartments as outlined by Teodoru and Wehrli (2005): (I) Bazias to Orsova Bay; (II) Orsova Bay; and (III) Orsova Bay to Iron Gate I Dam (Fig. 6). Each compartment was considered a conservative system where the inflow and the primary production was balanced by sedimentary accumulation and the output.

(I) *Bazias-Orsova Bay*. For the first compartment, an inflow at Bazias of  $16 \text{ kt Si yr}^{-1}$  was calculated from the average  $1.8 \text{ mg Si g}^{-1}$  of the inflowing particle load of

$8,870 \text{ kt yr}^{-1}$  (Teodoru and Wehrli, 2005). As the bulk sedimentation rate on this section was 4× less than upstream of the dam (Table 2), 20% of the total inflow ( $3.2 \text{ kt Si yr}^{-1}$ ) was retained by sedimentation, whereas the rest was transported towards the dam. Sedimentary BSi accumulation in this compartment calculated from sediment cores is  $7 \text{ kt Si yr}^{-1}$  (Table 2). At  $3.2 \text{ kt Si yr}^{-1}$  originating from the inflow, the accumulation of another  $3.8 \text{ kt Si yr}^{-1}$  is required. *In-situ* production at an average flux of  $144 \text{ g Si m}^{-2} \text{ yr}^{-1}$  was responsible for a biogenic silica production of  $13.1 \text{ kt Si yr}^{-1}$ . About 25% of the total BSi source reached the sediments and the rest was transported towards the dam (Fig. 6).

(II) *Orsova Bay*. *In-situ* diatom production in Orsova Bay was previously calculated as  $1.6 \text{ kt Si yr}^{-1}$ . Inflow from the main stream was derived as follows: assuming a rather constant increase of BSi from km 1045 to km 981 and km 955 (just upstream of Orsova Bay), we estimated a BSi concentration of about  $2.6 \text{ mg Si g}^{-1}$  of the inflowing particle load of  $540 \text{ kt yr}^{-1}$  (Teodoru and Wehrli, 2005) resulting in an input of  $1.4 \text{ kt Si yr}^{-1}$ . Sediment cores of Orsova Bay, with an average Si concentration of  $5.6 \text{ mg Si g}^{-1}$  (Table 1), revealed a total sedimentary Si accumulation of  $0.9 \text{ kt Si yr}^{-1}$ . Using the same concentration of  $5.6 \text{ mg Si g}^{-1}$  of the outflowing particle flux of  $375 \text{ kt yr}^{-1}$  (Teodoru and Wehrli, 2005), up to  $2.1 \text{ kt Si yr}^{-1}$  were calculated to be exported towards the dam. This means that 30% of the total load in Orsova Bay (inflow plus diatom production) was removed by sedimentation.

(III) *Orsova Bay – Iron Gate I Dam*. The input from the first compartment was  $20.7 \text{ kt Si yr}^{-1}$ . Additional sources



**Figure 6.** Schematic representation of BSi loads in the three main compartments of Iron Gate I Reservoir. For each compartment, an input, a primary production (PP), accumulation, and an output load was calculated.

were Orsova Bay at 2.1 kt and *in-situ* diatom production at 1.3 kt Si yr<sup>-1</sup>. Two main sinks were sediment accumulation and outflow at 11.1 and 13 kt Si yr<sup>-1</sup>, respectively (Fig. 6). Due to the high sedimentation rate in this compartment, up to 46% of the total Si source was accumulated behind the dam.

Model calculations indicated increasing sediment retention of BSi towards the dam. Compared to DSi inflow at Bazias of 396 kt Si yr<sup>-1</sup> calculated by Friedl et al. (2004) or 460 kt Si yr<sup>-1</sup> by McGinnis et al. (2006) (different calculation procedures resulted in slightly different values), the present retention of 19 kt Si yr<sup>-1</sup> represents only 4 to 5% of the total load. With its present storage capacity, the reservoir does not act as an important Si sink. One question is still open, however: is this low present Si retention in Iron Gate I representative of the last decades or did BSi burial change over time? The dynamics of BSi retention can be reconstructed from dated sediment cores.

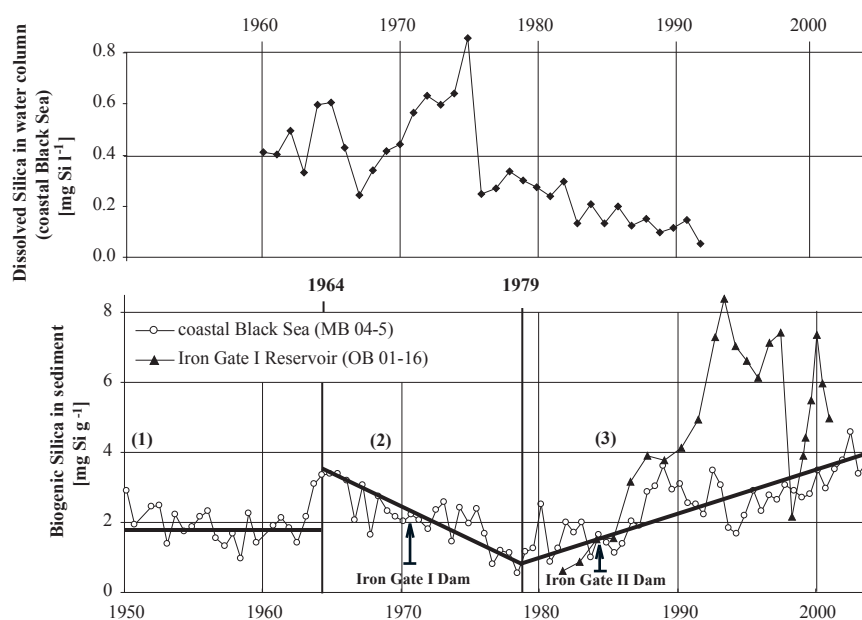
### BSi accumulation before and after closing the Iron Gate

High deposition rates in Iron Gate require quite long cores for covering the early stages period of the reservoir. At a length of 95 cm, the longest Iron Gate I core from Orsova Bay (OB 01-16) represents the deposition history of 19 years (1982–2001). To reach back to the completion of Iron Gate I in 1971, a core upstream of the dam must penetrate a substantial layer of over 7 m. As such a long sediment core is difficult to obtain, interpreting the past BSi

deposition in the reservoir was restricted to 1980, about 10 years after the construction of Iron Gate I dam.

Situated on the major bay of the reservoir where the sedimentary BSi deposition is dominated by *in-situ* diatom production, the longest core of Orsova Bay (OB 01-16) was considered typical for reconstructing BSi deposition. The down-core profile shows a general increase from low values of 0.5 mg Si g<sup>-1</sup> in 1982 to 5.5 mg Si g<sup>-1</sup> in 2001 (Fig. 4b, Fig. 7). As discussed above, BSi dissolution does not play an important role in the Iron Gate. Therefore, the increased BSi concentration over the last 20 years can be interpreted as a combined effect of enhanced diatom production and dilution effect due to a possible decrease in total suspended solids accumulation (Teodoru and Wehrli, 2005). The increase in diatom production may also be explained by a reduction in particle loads and therefore, decreased turbidity and not necessarily by increased DSi inflow. As the highest BSi concentrations were found in the youngest sediment layers of the reservoir representing a present-day BSi accumulation of 19 kt Si yr<sup>-1</sup>, the past retention capacity of Iron Gate I was probably lower. Increasing sediment retention by dams in the headwaters (Teodoru and Wehrli, 2005) might result in a more effective BSi removal than the Iron Gates.

The coastal Black Sea sediment (MB 04-5) showed three distinct patterns over the last 50 years. Dissolved silica concentrations measured by Cociasu et al. (1996) at the coastal waters of the Black Sea were added for comparison (Fig. 7): (1) a constant concentration of about 2 mg Si g<sup>-1</sup> for sediments deposited before the industrial



**Figure 7.** Si concentration measured in the sediments of Orsova Bay (OB 01-16) and coastal Black Sea (MB 04-5) and corresponding dissolved silica concentration measured in the Black Sea coastal waters (after Cociasu et al., 1996).

development in the Danube Basin countries of early 1960s; (2) an increase by almost a factor of two around 1962–1964 followed by a decrease from 3.5 to 0.5 mg Si g<sup>-1</sup> between 1965 and 1980; and (3) a gradual increase over the last 25 years from 0.5 mg Si g<sup>-1</sup> to over 4 mg Si g<sup>-1</sup> in 2004. The increase in the beginning of the 1960s can be seen as the onset of coastal eutrophication. This period was characterised by an 2.5 increase in diatom blooms whereas non-diatom phytoplankton increased by a factor of six (Humborg et al., 1997). For the same period, the coastal Black Sea waters showed a two-fold increase in dissolved silica concentration by (Cociasu et al., 1996, Fig. 7). The second pattern dominated by a general decrease in sedimentary BSi concentration was postulated to be caused by a reduced riverine Si load due to high diatom retention in the Iron Gates (Cociasu et al., 1996; Humborg et al., 1997). According to Cociasu et al. (1996), this period corresponded to an increased water column dissolved silica concentration (Fig. 7). Note that the decrease from 3.5 to 0.5 mg Si g<sup>-1</sup> observed in the sediments of Musura Bay started around 1965 ± 4, slightly earlier than completion of the Iron Gate I Dam in 1971. It is not surprising that the BSi decrease in the Black Sea sediments is not strongly correlated with closing of the Iron Gates as the total reduction in DSi load behind this dam is only 5%. Moreover, dam building activities in the headwaters of the Danube and tributaries extended over several decades (1945–1980).

In general, the decrease in BSi from early the 1960s to beginning of the 1980s at coastal Black Sea can be interpreted as a combined effect of: (i) dilution due to a general increase of non-siliceous phytoplankton blooms (Humborg et al., 1997) caused by increased nitrogen and phosphorus loads; and (ii) changes in sedimentation regime and suspended solids load.

Corresponding to a general decrease in dissolved silica concentration in the water column, the increase in sedimentary BSi concentration at the coastal Black Sea from the early 1980s until 2004 correlates well to measured BSi increased in sediments of Iron Gate (Fig. 7). This parallel increase contradicts the hypothesis of a strong inter-relationship between Si retention in the reservoir and Black Sea diatom limitation. If the hypothesis was true, an increased Si concentration in sediments of Iron Gate would have depleted Si concentrations at the coastal Black Sea.

One possible explanation for the higher BSi concentration at both sites is an increased diatom production in the river and the estuarine system due to reduced turbidity accompanied by a dilution effect due to reduced sedimentation flux of suspended solids. Thus, dam building activities over the last decades probably reduced the overall particle load of the Danube, considerably improving the light regime for diatom blooms (Teodoru and Wehrli, 2005).

## Conclusions

The results of this study confirmed that the largest reservoir on the Danube, Iron Gate I Dam, did not play a major role in Si retention. This suggests that damming of the river headwaters and tributaries exert a stronger cumulative impact on downstream ecology and nutrient transport than the construction of a single large impoundment. These findings are supported by the following observations:

(i) Sedimentary Si accumulation within Iron Gate I Reservoir during 2001 was 19 kt Si yr<sup>-1</sup> and is about 30× lower than postulated previously (Humborg et al., 1997) accounting for only 5% of the incoming DSi load at Bazias. *In-situ* diatom production within the reservoir was responsible for fixing up to 16 kt Si yr<sup>-1</sup>. Productivity was 3× higher in side bays compared to the main channel. Limited by a small area compared to the total reservoir surface, side bays were responsible for only 10% of total Si fixation.

(ii) Down-core Si profiles allowed reconstructing historical accumulation rates. With lower Si retention in the past compared to the recent situation, Iron Gate I Reservoir could not have caused a dramatic Si depletion in the Danube before reaching the Black Sea. Moreover, an in-phase increase in BSi concentration observed over the last 20 years in sediment cores from Iron Gate and the Black Sea suggests that additional factors such as lower turbidity due to upstream sedimentation and related concentration effects were responsible for increasing sedimentary BSi concentrations.

(iii) The decrease of BSi concentration in Black Sea sediments started slightly earlier than closure of Iron Gate I Dam. The historical record of dam construction over the last 50 years in the catchment suggests that the large number of impoundments on the Danube and its tributaries changed Si transport to the coastal Black Sea.

In general, this study implies that in the assessment of nutrient retention along a river system, the cumulative effect of a large number of dams must to be reconsidered.

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