change observed. Taken together, these data suggest that NADW flow attained levels similar to today 3–4 Myr ago, with a gradually increasing contribution from LSW, in particular after 2 Myr. Palynological evidence suggests that the near-surface Labrador current was not established until 1.8 Myr, consistent with increased convection at that time[28].

This study demonstrates the utility of long-lived radiogenic isotopes as tracers of water mass movement. Our results indicate that the isotopic signal associated with NADW strengthened around 3–4 Myr ago, with a gradually increasing contribution from water sourced in the Labrador Sea, and suggest that the present global thermohaline circulation pattern was not established until that time. These data cannot distinguish between increased erosional input into the Labrador Sea or increased deep-water formation in the same area. However, recent model simulations[29] provide support for an increased rate of deep-water formation in the Labrador Sea following closure of the Central American Isthmus. This result, when taken with our findings, supports the conclusion that isthmus closure had a major effect on circulation and climate. ☐

Received 25 October 1996; accepted 3 February 1997.

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**Acknowledgements.** We thank H. Buckley, Natural History Museum, London for assistance and provision of the sample studied here; S. Reed for assistance with the microprobe analysis; B. Bourdon, G. Henderson, A. Cohen, and F. von Blanckenburg for discussions; and K.W.B. thanks C. J. Allègre for providing the time and support to finish this study. This work was supported by the NERC and the Royal Society.

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# Effect of Danube River dam on Black Sea biogeochemistry and ecosystem structure

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**Rivers contribute significantly to the pollution and eutrophication that have caused drastic changes to the ecosystem of the Black Sea[1–3]. Although damming is known to affect riverborne nutrient loads, and thus riverine ecosystems, evidence for significant effects in open coastal waters is sparse[4–6]. Here we present long-term data sets of water and nutrient discharge from the River Danube to the Black Sea. These data reveal a reduction in the dissolved silicate load of the river by about two-thirds since dam constructions in the early 1970s. A concomitant decrease in wintertime dissolved silicate concentrations by more than 60% was observed in central Black Sea surface waters. The consequent changes in silicon to nitrogen ratio of the Black Sea nutrient load appear to be larger than those caused by eutrophication alone, and seem to be responsible for dramatic shifts in phytoplankton species composition from diatoms (siliceous) to coccolithophores and flagellates (non-siliceous). Our results strongly suggest that the damming of the Danube has been instrumental in causing the observed changes in Black Sea surface waters[3,7–9], and that the large number of dams in operation around the world today could similarly affect the food web structure and biogeochemical cycling in coastal seas.**

Human interventions have caused a worldwide increase in river inputs of nitrogen (N) and phosphorus (P) to the coastal seas by more than a factor of four, leading to considerable eutrophication[10,11] and to an increase in the frequency of unusual and/or noxious algal blooms[12]. Shifts from diatoms to non-siliceous phytoplankton in the receiving waters of the Mississippi and the Rhine have been attributed to a change in Si:N:P ratios[4,12–14] caused by excess of N and P, that is, cultural eutrophication. The construction of dams in rivers can also cause considerable reductions in nutrient loads owing to the removal of these nutrients in reservoir sediments (the 'artificial-lake effect')[5]. Whereas this removal might be overcompensated by anthropogenic nitrogen and phosphorus inputs downstream of the reservoir, no such compensation has been observed for silicate, for example, in the Nile[5].

The River Danube, which contributes ~70% of the river inputs into the Black Sea, was dammed in 1970–72 approximately 1,000 km upstream at the Yugoslavia/Romania border by the 'Iron Gates' causing significant changes in the Danube's discharge pattern[15]. Annual maxima in Danube water discharge and silicate concentration in spring deviates from the general trend observed in pristine rivers (Fig. 1), where silicate concentrations show very little temporal and regional variations probably due to buffering processes involving silicium-containing minerals (clays)[16,17]. Spectral analysis (Fig. 2) of the Danube data shows that the annual frequency band revealed the highest variance densities of water discharge and silicate concentration; both variables are highly coherent ($k = 0.86$, see Table 1). Thus, the concentration of silicate and other nutrients can be expressed as a function of water discharge (Table 1). Furthermore, a phase displacement of about one month ($\sim$30 days) occurs, whereby silicate leads the water discharge. These two effects can be attributed to the pattern of reservoir operation. To prevent spring floods, the water stored in the reservoir is released through the outlets of the dam before maximum water levels are reached. Thus, nutrient-enriched reservoir waters flow into the Black Sea shortly before the annual peak in water discharge.

As well as the temporal variability in silicate discharge, the retention of silicate in the reservoir has led to an overall decrease

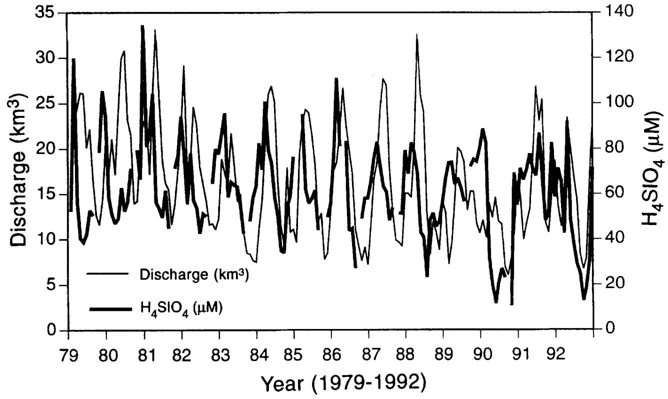

**Figure 1** Silicate concentration (monthly means) and discharge (monthly means) of the River Danube from 1979 to 1992. The silicate time-series station (daily measurements) is located at the mouth of the Sulina branch of the Danube delta. Water discharge was measured ~60 km upstream of the river mouth, where the Danube enters the delta. Silicate samples were filtered through polycarbonate filters (0.2 μm) and frozen in 100-ml polyethylene bottles before being analysed by colorimetry[18].

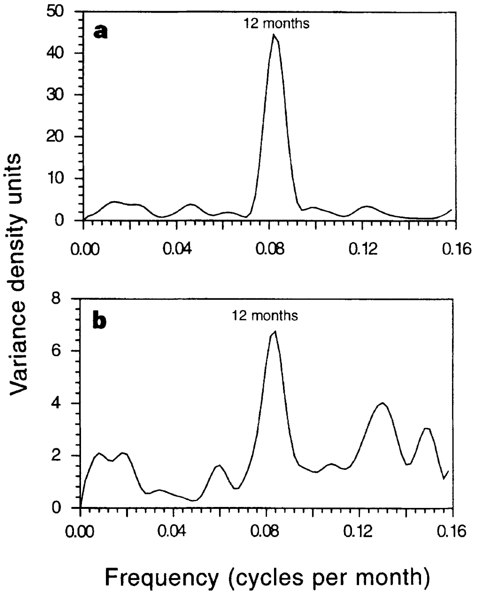

**Figure 2** Variance density spectra of discharge (**a**) and silicate (**b**) time series 1979-92. Silicate data (monthly means) and water-discharge data (monthly means) were studied by time-series analysis to evaluate the statistical relationships between those time dependent variables. Spectral and cross-spectral analyses (Blackman-Turkey technique as used by Hays *et al.*[27]; records filtered by cyclonic convolution procedures according to Mesko[28]) of various time series were performed. Spectral analysis transforms the time series into a spectrum of dominant frequencies, where the variance spectrum represents the contribution of the whole variance spectrum over a specific frequency. It is therefore a relative measure of the amplitude of the dominant frequency of each specific time series. Main periodicities are indicated. Cross-spectral analysis for other nutrient variables is given in Table 1.

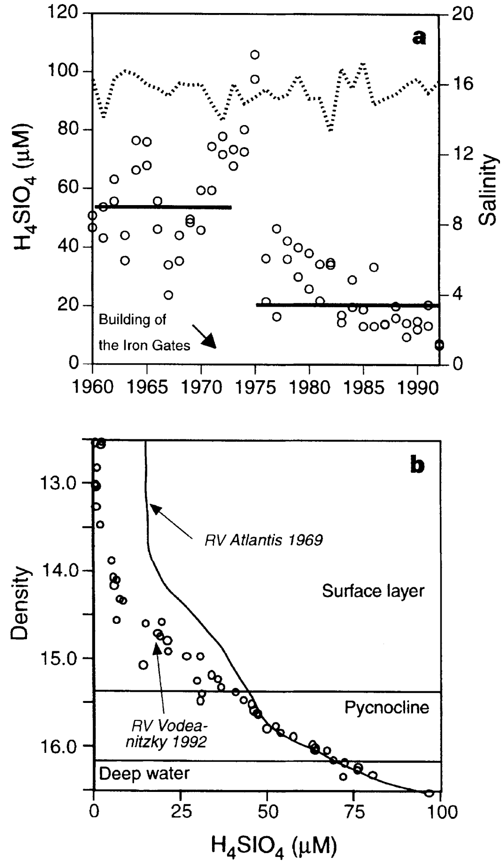

**Figure 3** Silicate concentrations in the Black Sea. **a**, Mean winter silicate concentrations (open circles) at Constanta station (January and February, daily measurements); the bold lines gives the overall medians 1960-72 and 1973-92. Samples were measured directly after sampling using colorimetry[29,30]. This time-series station is located about 60 nautical miles south of the Danube mouths. The salinity between 1960 and 1992 at Constanta station in winter (January and February, also daily measurements) has remained at about $S = 15$ (dashed line), indicating that the Danube influence on salinity has remained constant over time. **b**, Composite profiles of silicate plotted against density. Open circles, data from 7 stations of the 1992 RV *Prof. Vodeanitzky* (October); solid line, data from 1969 RV *Atlantis II*[9,24] (March-April). The surface layer in the central part of the Black Sea extends to the permanent pycnocline (a steep density gradient where density increases by $\sim 1\sigma_t$ within a few tens of metres) and corresponds to about 100 m water depth. Note that both the 1969 and 1992 data display conditions when dissolved inorganic nitrogen was depleted in the surface layer. Density was measured *in situ* with a Mark III CTD (conductivity, temperature and depth) instrument. Silicate was measured directly on-board by colorimetry[29].

in its concentration. The median silicate concentration for the period 1979–92 of 58 $\mu$M for the Danube (Fig. 1) is far less than the concentration of $\sim$140 $\mu$M derived from total discharge figures given by Almazov[18] from measurements made during several cruises in 1959–60. These are the only data available before the construction of the 'Iron Gates' and show that the annual silicate load dropped from $800 \times 10^3$ tons (assuming Si is present as $H_4SiO_4$) in 1959–60[18] to (230–320) $\times 10^3$ tons today[1]. Winter concentrations of silicate in coastal waters covering the period 1960–92 decreased proportionally from 55 $\mu$M before the dam was built to 20 $\mu$M after its construction (Fig. 3a), which is in good agreement with the historical measurements given by Almazov[18]. Altered nutrient concentrations at this coastal station are clearly governed by the Danube river and in the case of nitrogen and phosphorus are only little influenced by coastal sources[1]. The strong decrease in the Si:N ratio from 42 to about 2.8 can be attributed also to the concomitant rise in dissolved inorganic nitrogen caused by the increased Danube inputs (nitrate concentration at this coastal station increased from a median value of $\sim$1.3 $\mu$M in the early 1960s to a median of 7.9 $\mu$M in the 1980s)[1].

These altered nutrient inputs have resulted[19] in a distinct increase in phytoplankton bloom frequency, in cell densities and in the number of bloom-forming species from the beginning of the 1970s (Table 2). While diatom blooms increased by a factor of 2.5, blooms of non-diatoms such as dinoflagellates, the prymnesiophytes *Emiliania huxleyi* (coccolithophore) and the facultative toxic species *Chromulina* sp., as well as the Euglenophyte *Eutreptia lanowii*, increased by a factor of six. In our observations[20] in 1993, we found $140 \times 10^6$ cells $\text{l}^{-1}$ of *Emiliania huxleyi* near the Danube plume at salinities as low as 10. Before the construction of the dams, blooms of coccolithophores were only reported from regions far offshore and later in the season[21]. The effect of the 'Iron Gates' on phytoplankton assemblages can be demonstrated by the following calculations: the annual increase of dissolved inorganic nitrogen load of the Danube since the early 1970s is estimated[1] to be $\sim 3.6 \times 10^{10}$ mol. Assuming Si:N ratios of 0.65 for *Skeletonema costatum*[22], the predominant diatom species in the area (Table 2), a silicate uptake of $\sim 2.3 \times 10^{10}$ mol would be required to remove this nitrogen. Remarkably, this corresponds to the amount of silicate which is being retained in the reservoir each year ($2.1 \times 10^{10}$ mol). This implies that a large part of the past and future increase in nitrogen loads of the Danube after damming of the river are being (and will be) removed by non-diatom species.

The effect of silicate decrease is also seen in the central Black Sea, where the depth of the mixed layer varies both seasonally and regionally[3], and diffusion and mixing along the isopycnal surfaces is rapid[23]. We compare silicate concentrations from 1992 with historical data from the RV *Atlantis II* expedition in 1969[9,24] by plotting silicate against density (Fig. 3b). Both were measured in periods of nitrogen depletion, when biological removal of silicate was at its limit. This comparison shows an order of magnitude decrease in silicate concentration, as was also reported in surface waters for 1988 (June–July) in the entire central Black Sea[9].

**Table 1 Phase relationships of water discharge and nutrients**

| Variable | Phase displacement | | Coherency | Zero-coherency | *T* |
|---|---|---|---|---|---|
| | $\phi$ (°) | months | | | |
| Discharge/$NO_2$ | 26.7 ± 19.8 | 0.90 | 0.78 | 0.64 | 168 |
| Discharge/$NH_4$ | 26.1 ± 30.8 | 0.88 | (0.60) | 0.64 | 156 |
| Discharge/$PO_4$ | 22.7 ± 20.4 | 0.78 | 0.77 | 0.64 | 168 |
| Discharge/$H_4SiO_4$ | 29.8 ± 15.1 | 0.98 | 0.86 | 0.64 | 168 |

Phase relationships of cross-correlated variables (water discharge and nutrients) at the 12-month (annual) frequency band are given. Cross-correlation analyses the relationship of the different time-dependent variables; dominant frequencies of each variable and their phase relationships are studied. Phase displacement is described as the angle $\phi$, which represents the contribution over a whole 360°-cycle. Coherency between two variables represents the correlation within the frequency domain, and is a common method of evaluating the statistical relationships of data sets within the time domain. Items tabled are: phase displacement ($\phi$) with 80% confidence interval; phase displacement in months coherency ($k$), entry in brackets indicates that cross-correlated variables are not coherent; 80% test statistics for non-zero coherency ($k_0$); and length of the time series ($T$) in months. Positive phases mean that the second variable leads the first variable. Cross-correlation of nitrate and water discharge was not carried out owing to the lack of sufficient numbers of nitrate measurements.

The observed decrease above the pycnocline (corresponding to a depth of $\sim$100 m) since 1969 amounts to $\sim$1,500 mmol $\text{m}^{-2}$ or $14.7 \times 10^6$ tons for the entire central basin. The total retention of silicate by the 'Iron Gates' of $\sim 11.8 \times 10^6$ tons since the construction of the dams in the early 1970s makes up 80% of this total decrease. Similar effects by dams on silicate discharge of the rivers are conceivable also for the Dnepr and Dnestr[25], which contribute to $\sim$20% of river water input into the Black Sea. Thus, by far the largest part of the silicate reduction in the central basin appears to be caused by dam constructions around the Black Sea.

The long-range effect of the Danube is corroborated by data on barium (Ba) and radium ($^{226}$Ra) depletion in the Black Sea surface waters[8]; both these species are proxies for silicate. Model calculations[8] implied that biological forcing, that is, sedimentation of diatoms, is primarily responsible for the decrease in Ba and $^{226}$Ra (and thus for the decrease in silicate) in the central Black Sea over the past 30 years. However, satellite-derived chlorophyll data (coastal zone colour scanner data from 1,177 scenes, 1979–1982; EU Joint Research Centre) demonstrate that intense blooms (average chlorophyll concentrations, 3–10 mg $\text{m}^{-3}$) occur mostly in nearshore areas of the northwestern shelf, whereas in the central parts they do not exceed 0.5 mg $\text{m}^{-3}$. Moreover, Ba fluxes measured with sediment traps were lower by a factor of 10 than the model-predicted flux[8,21]. The estimated decrease in Danube silicate inputs could account for this reported discrepancy.

Our results show that water and sediment storage in reservoirs behind the 'Iron Gates' have altered the biogeochemistry not just of the river and the adjacent coastal waters, but also of the entire Black Sea basin. The observed species shift towards carbonate-producing coccolithophores in the coastal waters (most certainly caused by decrease in silicate) exerts significant control on seawater chemistry such as alkalinity and pH. Furthermore, the occurrence of potentially

**Table 2 Phytoplankton concentration in the northwestern Black Sea**

| | 1960-70 | | 1980-90 | |
|---|---|---|---|---|
| | Cell densities ($10^6$ cells $\text{l}^{-1}$) | Number of blooms | Cell densities ($10^6$ cells $\text{l}^{-1}$) | Number of blooms |
| *Skeletonema costatum* | 10-18 | 3 | 10-90 | 8 |
| *Skeletonema subsalsum* | – | – | 10-19 | 2 |
| *Cyclotella caspia* | – | – | 23-300 | 2 |
| *Chaetoceros similis* | – | – | 22 | 1 |
| *Cerataulina pelagica* | – | – | 5-6 | 3 |
| *Nitzschia delicatissima* | 6-21 | 4 | 17 | 1 |
| *Nitzschia closterium* | – | – | 13 | 1 |
| *Nitzschia tenuirostris* | – | – | 75 | 1 |
| *Leptocylindrus danicus* | 7 | 1 | – | – |
| Total diatoms | 7-21 | 8 | 5-300 | 19 |
| *Prorocentrum cordatum* | 17-51 | 4 | 10-810 | 9 |
| *Prorocentrum scutellum* | – | – | 7 | 1 |
| *Scripsiella trochoidea* | – | – | 26 | 1 |
| *Heterocapsa triquetra* | – | – | 5-12 | 3 |
| Total dinoflagellates | 17-51 | 4 | 5-810 | 14 |
| *Eutreptia lanowii* | – | – | 5-108 | 6 |
| Total Euglenophytes | – | – | 5-108 | 6 |
| *Emiliania huxleyi* | – | – | 220-300 | 2 |
| *Chromulina* sp. | – | – | 1,000 | 1 |
| Total prymnesiophytes | – | – | 220-1,000 | 3 |
| Total blooms | | 12 | | 42 |

Blooms are defined here as $> 5 \times 10^6$ cells $\text{l}^{-1}$. Phytoplankton samples were taken[19] daily at Constanta station, and monthly at offshore stations from different areas of the Romanian shelf. Cell counts were obtained by inverted microscopy. A dash indicates that the organism was absent.

toxic flagellate blooms may become more frequent, as observed in other coastal areas. Similar effects may be expected for the central Black Sea where, in contrast to pre-dam conditions, silicate depletion appears now to be more frequent. The combined effect of the altered silicate inputs from the Danube, overfishing and of the introduction of alien species such as ctenophores[2] on food-web structures is yet to be investigated. Our results further imply that other changes observed in the Black Sea, such as the spreading of the suboxic zone towards the surface[9] or the increase in nitrate concentrations above the pycnocline[7], may be related to alterations of the Danube input.

Today more than 36,000 dams are in operation around the world and more are being constructed at an appreciable rate[26]. Though the observed effects of these dams can be expected to be more severe in closed seas (such as the Black Sea) than in rivers feeding into open systems, these effects could be of global consequence. ☐

Received 25 June 1996; accepted 5 February 1997.

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**Acknowledgements.** We thank U. Struck and S. Podewski for statistical analyses; J. Murray for comments on the manuscript; L. Popa and L. Dorogan for parts of the nutrient determinations; S. Kempe and A. Reimer for cruise coordination; and U. Horstmann for encouragement and support. This work was supported by the German Volkswagen Foundation and the EU EROS (European River Ocean Study) Black Sea Programme.

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# Evidence for a selectively favourable reduction in the mutation rate of the X chromosome

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**The equilibrium per-genome mutation rate in sexual species is thought to result from a trade-off between the benefits of reducing the deleterious mutation rate and the costs of increasing fidelity[1,2]. We propose that selection will often favour a lower mutation rate on the X chromosome than on autosomes, owing to the exposure of deleterious recessive mutations on hemizygous chromosomes. We tested this hypothesis by examining 33 X-linked genes that have been sequenced in both mouse and rat, and compared their rate of evolution against 238 autosomal genes. The X-linked genes were found to have a significantly lower rate of synonymous substitution than the autosomal genes. Neither the supposed higher mutation rate in males nor stronger purifying selection against slightly deleterious mutations on the X chromosome can account for the low value. The most parsimonious explanation is that rodents have a lower mutation rate on the X chromosome than on autosomes. It is therefore likely that previous indirect estimates of the excess male mutation rate are inaccurate. Indeed, after correction we find no evidence for a male-biased mutation rate in rodents. Furthermore, the rate of synonymous substitution in Y-linked genes is not significantly different from that in autosomal ones. The extent to which enhanced male mutation rates are problematic[3] for the mutational deterministic model[4] of the evolution of sex must, in turn, be questioned.**

The evolution of mutation rates is governed by two opposing forces: the costs imposed by deleterious mutations, and the ability to adapt to a changing environment[1,5]. In contrast to asexual populations, selection acting within a sexual population will always favour a mutation rate of zero[1]. That this is not observed can be accounted for by supposing that there is a trade-off between the benefits of reducing the deleterious mutation rate, and the costs imposed by increasing fidelity (such as the time and energy spent proof-reading)[1,2]. Alternatively, there might be a physiological limit to the degree of accuracy in DNA replication, or perhaps group selection favours those lineages capable of producing new mutations and hence adapting.

The trade-off theory predicts that the selection acting on a modifier of mutation rates is proportional to the strength of selection against a mutant allele. Owing to the exposure of deleterious recessive mutations on hemizygous chromosomes, it follows that the selective advantage of an unlinked modifier reducing the mutation rate of the X chromosome can, under many circumstances, be much higher than that of a modifier reducing the autosomal mutation rate by the same factor (Fig. 1 and Box 1). This need not always be true. In mammals, more mutations are thought to occur in the male germ line than in the female[6]. As the proportional excess male mutation rate ($\alpha$) increases, so the number of deaths imposed by new mutations on autosomes and on the X will tend to be comparable, as autosomes spend more time in males than does the X chromosome. Further, as the strength of selection on the modifier depends on the number of loci under its influence, a reduced mutation rate on the X chromosome is more likely in organisms with proportionally large X chromosomes and a