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Modelling the Transfer and Retention of Nutrients in the Drainage Network of the Danube River

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The Danube catchment basin (817 000 km^2, 76 × 10^6 inhabitants) is the major freshwater contributor to the Black Sea (6300 m^3 s^{-1}, 80% of the annual river discharge into the north-western Black Sea). The aim of the modelling approach developed for the Danube River, is to establish how land use and management of the whole watershed are linked to nutrient (N, P, Si) delivery and retention by the river. The approach uses an adaptation of the RIVERSTRAHLER model, which is based on a schematic representation of the drainage network deduced from geomorphological analysis by stream orders. The whole catchment was divided into 10 sub-basins and one branch, to provide a description satisfying both the need to take into account the heterogeneity of the system and the availability of constraints and validation data. On the basis of this description, a hydrological model was developed, which adequately simulated the seasonal variations of the discharge measured at the outlet of the basin. The model itself resulted from the coupling of the hydrological model with a biogeochemical model (RIVE), which takes into account the main ecological processes. It established a link between microscopic processes, their controlling factors and their macroscopic manifestations in terms of nutrient cycling and ecological functioning at the scale of the whole drainage network. The model was validated for the period from 1988 to 1991 on the basis of available observations of the major water-quality variables involved in the eutrophication processes (inorganic nutrients, phytoplankton biomass, dissolved oxygen, etc.). A reasonable agreement was found between the simulations of the model and the observations. Nutrient fluxes to the Black Sea, calculated for our reference period, are in the same range as those obtained via other approaches. Si/P and N/P ratios suggest silicon, rather than phosphorus, limitation for diatoms and phosphorus, rather than nitrogen, limitation for overall phytoplankton in the coastal zone of the Black Sea. The sharp drop in N and P delivery to the Black Sea, observed since 1991, was simulated with a scenario constructed to reproduce new constraints based on documented modifications of human activity in the watershed. Due to the scarcity of data, there is a need for further validation of the model. Nevertheless, the structure of the model allows the specificity of each sub-basin to be taken into account in future management plans.

Keywords: modelling; nutrient transfer and delivery; nutrient retention; Danube Basin

Introduction

Coastal eutrophication and its associated undesirable algal blooms and modifications of the marine food-webs are known to be the result of increased and unbalanced riverine delivery of nutrients (N, P and Si) (Officer & Ryther, 1980; Billen *et al.*, 1991; Conley *et al.*, 1993; Billen & Garnier, 1997). The north-western shelf of the Black Sea offers a dramatic example of a coastal area whose ecological functioning has been strongly affected by coastal eutrophication during the last few decades (Mee, 1992). The observed changes have been related to the long-term trends of nutrient delivery by the Danube River (Cociasu *et al.*, 1996; Humborg *et al.*, 1997). In order to understand these trends, and to manage nutrient load, a model must be built to relate nutrient riverine delivery to the different land-based sources in the catchment and to the numerous processes—transfer, retention and elimination—that modify the nutrient loading during the downstream travel of the water masses through the whole drainage network.

The RIVERSTRAHLER model (Billen *et al.*, 1994; Garnier *et al.*, 1995) is one of the few available tools for modelling nutrient cycling and ecological functioning of entire drainage networks as a function of the properties of their watershed. The basic assumption in the RIVERSTRAHLER model is that of the unicity of the microscopic processes (biological and physico-chemical) involved in the functioning of river systems, which implies that the kinetics of the processes are the

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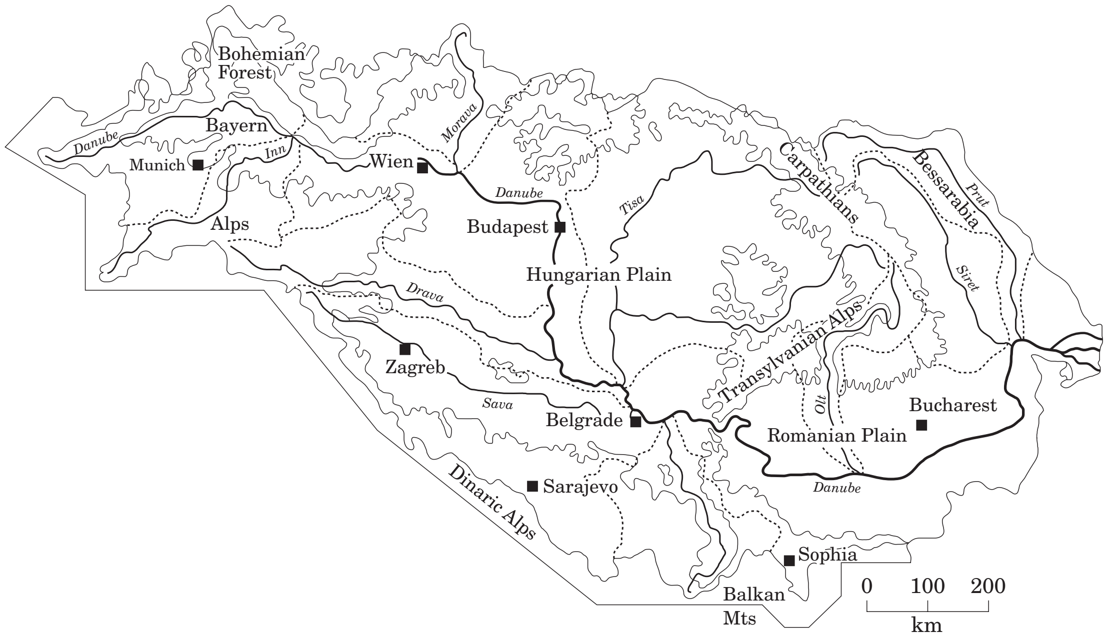

FIGURE 1. The Danube basin: geographical characteristics and boundaries of sub-basins (dotted lines).

same from headwaters to downstream sectors, while the hydrological and morphological processes controlling their expression differ widely along the upstream–downstream gradient, as do the constraints due to inputs from point and diffuse sources. Therefore, the specificity of the ecological structure and function of the different sectors of the river continuum resides in the constraints, rather than in the nature of the processes involved. The RIVERSTRAHLER model takes into account the whole drainage network according to the concept of stream orders (Strahler, 1957): the complex network of tributaries is represented by a regular scheme of the confluence of rivers of increasing stream orders with mean morphological characteristics. One obvious limitation of this approach is the fact that it only provides simulations of the mean behaviour of tributaries of given orders, instead of describing a real river with its own local characteristics. In order to improve the geographical resolution, it is possible to separately implement the approach to several sub-basins, and to connect the results to a model of the main branch of the drainage network. This strategy was adopted for the Danube River system, with the objective of understanding the budget of nutrient transfer into the Black Sea from land-based sources within the watershed.

Hydro-morphology of the Danube River

Morphology

With a catchment basin of 817 000 km^2, and a main course 2860 km long, the Danube River flows through many different geological facies and types of land-cover. From its source in the Black Forest to its mouth on the Black Sea, the Danube River receives the following: on its right bank, the tributaries Inn, Drava and Sava, originating in the Alps and the Dinaric Alps, as well as the Velika Morava flowing from the Balkans; and on its left bank, the major tributaries Morava, rising in the Bohemian Forest, and Tisza, originating in the Carpathians, but draining a large area of the Hungarian plain, and the Olt, Siret and Prut rivers, with sources in the Carpathians (Figure 1). To achieve a compromise between geographic resolution and model flexibility, we divided the Danube network into 10 sub-basins, corresponding to the main tributaries mentioned above and the upper Danube (which were all represented by their Strahler stream order structure), and the main branch of the Danube, from its junction with the Inn River to its mouth (Figure 1).

The morphological characteristics of the sub-basins required by the model include the mean value by stream order of the watershed area, length, slope, width and number of tributaries. For small catchments, this information can be determined by direct measurements on topographic maps with a proper scale (1:50 000) to show all first-order streams. This approach is impracticable for a basin the size of the Danube. Simplified procedures were therefore developed, based on the logarithmic relation existing for most river systems between morphological characteristics (number, length, width, slope, watershed area, etc.) and stream order (see Billen *et al.*, 1995, for a number of European rivers). For each of the

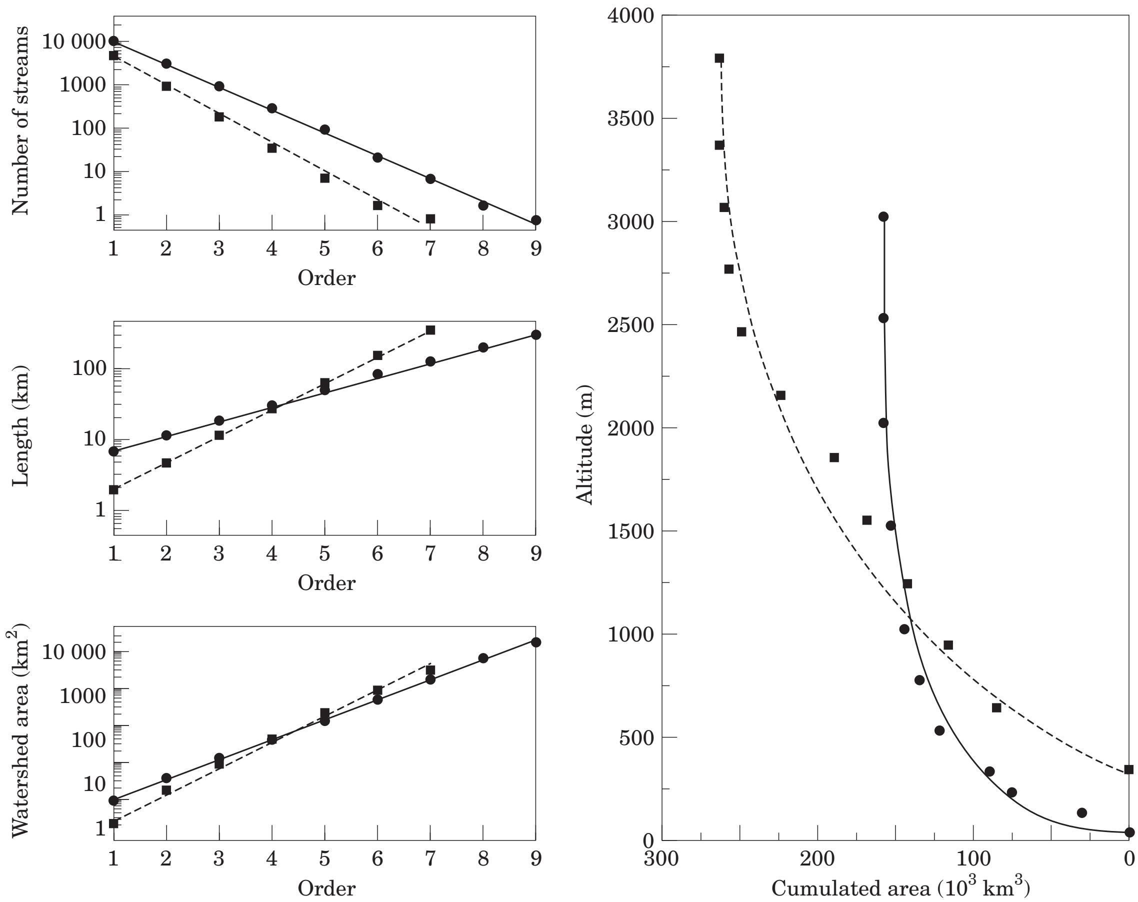

FIGURE 2. Comparison of morphological characteristics of two different sub-basins of the Danube River. Relationship between stream order and number of tributaries, length and watershed area. Hypsometric function fitted on empirical points. (●—●) Tisza; (■--■) Inn.

sub-basins considered in the Danube catchment, the characteristics of large tributaries (orders 4 and above) were determined on a digitized hydrological network from a map scaled 1:400 000; geomorphological characteristics of small stream orders were then obtained by extrapolation. The results are illustrated for two contrasting sub-basins (Figure 2). Values of mean slope for each stream were calculated from the hypsometric analysis of the watershed, also established from 1:400 000 maps (Hannon *et al.*, 1996).

As for the main branch of the Danube River, the main characteristics required by the model along the longitudinal profile are width and wetted section, characteristics of weirs and reservoirs, all special features influencing the residence time of the water masses, and, consequently, the ecological functioning of the system. Since 1950, to make the river navigable, 24 weirs have been constructed in the upper course of the river creating a succession of reaches. More recently, in 1994, a 25-km long canal was built parallel to the river downstream from Bratislava (pK 1870), diverting the totality of the Danube River discharge. Upstream of the canal, in the Gabcikovo reservoir, a 20–25-m high dike impounds a water volume of $240 \times 10^6\,m^3$ for hydroelectric power generation. Having flowed almost freely for 800 km, the Danube crosses the Carpathian mountains where two dams (Iron Gate I and II) were constructed in 1970 and 1984, respectively, for the dual purpose of navigation and hydroelectric power production. A sector of about 400 km of the river is affected by these dams. The lower course of the Danube River is free of navigation weirs until forming the delta and flowing into the Black Sea (Figure 3).

Hydrological regime and modelling hydrology

The average discharge of the Danube River into the delta amounts to $6300\,m^3\,s^{-1}$ (a specific discharge of $8\,l\,km^{-2}\,s^{-1}$), with extreme values from 2000 to $12\,500\,m^3\,s^{-1}$ (Annuaire Hydrologique du Danube, 1991). Due to high precipitation in the upstream

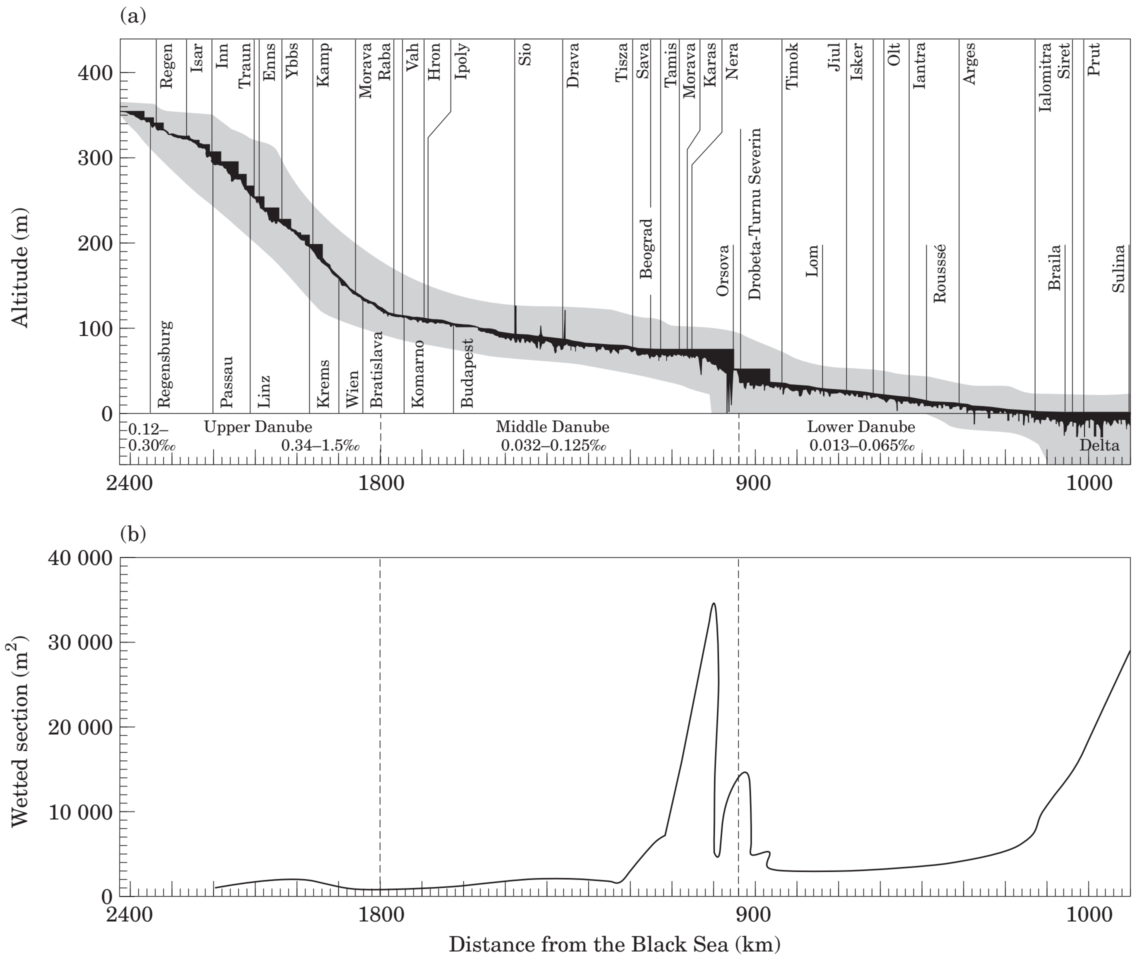

FIGURE 3. Morphological characteristics of the longitudinal profile of the Danube River. (a) Longitudinal profile of altitude and depth redrawn from Stancik *et al.* (1989). (b) Longitudinal profile of the wetted section.

alpine sector, the discharge is already high in Vienna (annual mean of about 2000 $m^3 s^{-1}$ and a specific discharge of no less than 19 $l km^{-2} s^{-1}$). The snow-cover on the watershed lasts from over 200 days in the highest mountain regions to about 10 days on the Black Sea coast, and the mean proportion of snow in the total annual precipitation ranges from 90% to 10–15%.

Except in a small sector of the upstream course of the Danube in the Black Forest, where an oceanic rainfall regime (with maximum discharge in winter) is observed, the highest discharge of the upper Danube occurs in the spring, or even at the beginning of summer, over most of its course (Guilcher, 1963). A clear minimum is observed in winter. Due to the influence of Alpine tributaries, its regime is of a glacier or snowmelt type upstream of Vienna (Ötzal glacier). Downstream, its hydrological regime becomes one of rainfall or snowmelt. Except in the upper Drava, the ice influence is very small. Therefore, maximum discharges shift to winter and minimum discharges in summer are lowered by evapotranspiration; a second maximum may be observed in autumn.

The HYDROSTRAHLER module calculates the hydrology of the whole drainage network from the morphological characteristics by stream order. Discharge in order N tributaries is calculated as the sum of the discharges of their two $N-1$ order tributaries, the discharges of lateral tributaries of order 1 to $N-1$, and the flow from its direct watershed, i.e. the part of the watershed that does not belong to the catchment of the affluents (see Billen *et al.*, 1994). The latter is calculated from precipitation and potential evapotranspiration data with a classical rain–discharge conceptual model, taking into account the role of a soil and an aquifer reservoir (see e.g. Bultot & Dupriez, 1976). This model, which involves four parameters (soil saturation, infiltration rate, internal flow rate and aquifer flow rate), distinguishes between three components of the discharge from the

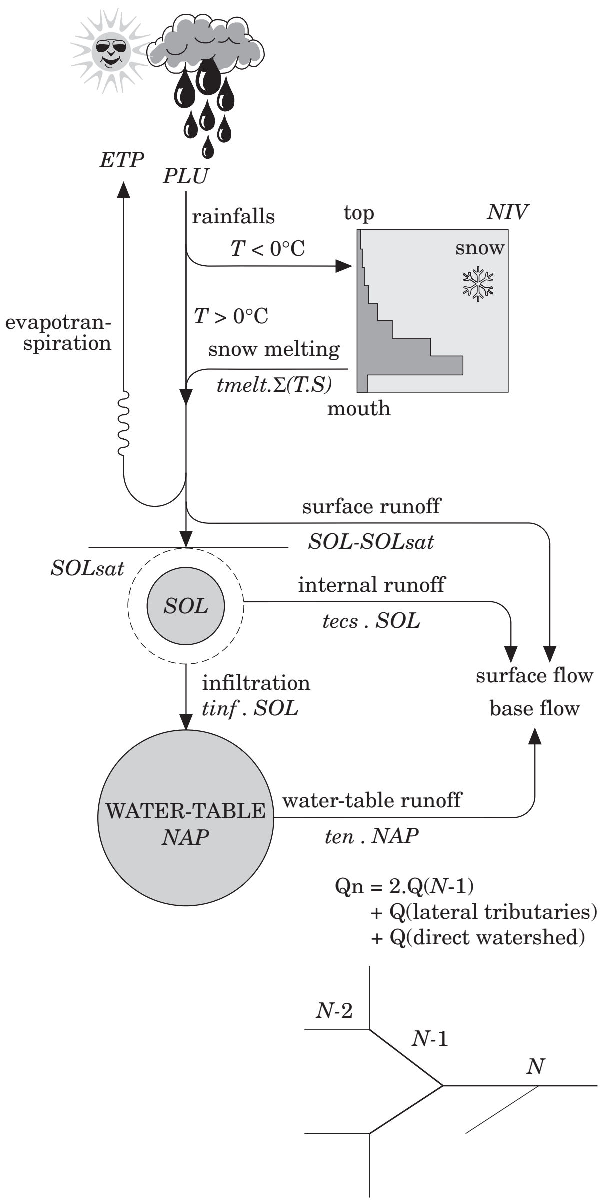

FIGURE 4. Schematic representation of the HYDRO-STRAHLER model and its parameters. NAP_0: initial level of the water-table (mm); SOLsat: water saturation level of the soil (mm); tinf: rate of infiltration (decade^{-1}); tecs: rate of superficial runoff (decade^{-1}); ten: Water-table runoff (decade^{-1}); tmelt: degree-decade factor (mm °C^{-1} decade^{-1}); NIV_0: initial snow depth (mm at the top of the basin).

watershed: the base flow supplied by the water table, the internal (or hypodermic) flow supplied by the soil reservoir and the surface runoff supplied in periods of soil saturation (Figure 4). As the Danube basin is strongly influenced by a snow regime on its upstream catchment, a model of snow and ice storage and melting, formulated as proposed by Martinec (1975) was added to this simple hydrological model (Hannon *et al.*, 1996). It is assumed that the snow coverage is 100% after a snowfall, and decreases linearly when the temperature becomes positive. A temperature gradient is taken into account (0·65 °C per 100 m) based on the hypsometric analysis of each sub-basin, divided into 10 altitude layers. The contribution to surface runoff by each layer is calculated from the formulation of Martinec (1975):

$$M = aT_dS$$

where M = the snowmelt depth (cm), a = the degree-day factor (cm °C^{-1} day^{-1}), T_d = the number of degree-days (°C day) and S = the relative snow cover. S is given by the expression

$$S = l - kd$$

where k = the linear snow cover decrease coefficient and d = the number of successive days with positive air temperatures. The total contribution by snowmelt to the surface runoff is given by the sum of the contributions from all layers, calculated from air temperature data collected at a meteorological station within the basin, corrected for the elevation.

In addition to the morphological description of the drainage network, the model thus requires the knowledge of seven hydrological parameters, as well as the initial values of the stocks, which are determined by adjustment of the simulated seasonal variations of discharge to values measured at the outlet of each sub-basin. Statistical parametrization software (Fahmy, 1994) determines the optimal values of these seven parameters, within reasonably set limits.

From the value of the discharge [Q, (m^3 s^{-1})] calculated by stream order, width [w, (m)], slope [s, (m m^{-1})], mean depth [d, (m)] and flow velocity [v, (m s^{-1})] are calculated by rearranging Manning's empirical formula (Billen *et al.*, 1994). The flow from the direct catchment area of the river, or from its lateral tributaries of lower stream orders, ‘ dilutes ’ the water masses flowing through the main channel. The corresponding dilution factor and its variations with the stream order and the season are very important for controlling the ecological functioning of rivers.

In the main branch of the river, the calculation is similar, taking into account the contribution to the flow of both the direct watershed and the considered sub-basins. In regulated sectors, the values of the depth and the wetted section are taken into account as described in Figure 4.

Because of the scarcity of available data (Annuaire hydrologique du Danube (1988–1991)), rainfall data were averaged for the 1988 to 1991 period (all four

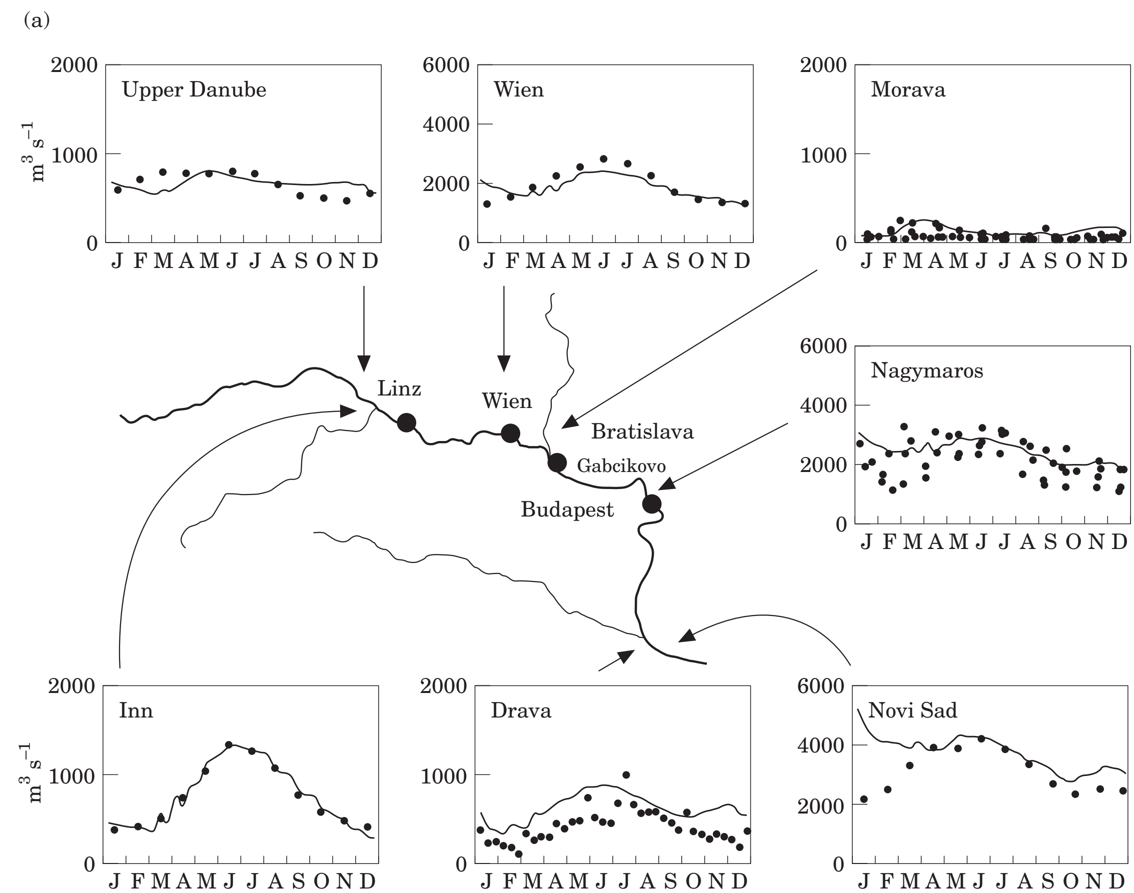

FIGURE 5. (a).

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were rather similar, dry hydrological years). Values of the discharges were pooled for validation. The simulations by the HYDROSTRAHLER model are generally in good agreement with the measured data [Figure 5(a,b)]. Major disagreements were found for the Sava sub-basin; the model overestimated the winter discharges. The model adequately simulates the differences in the hydrological regimes of the Danube River and its tributaries. The great contribution by the Inn tributary is of a glacier or snowmelt type, consequently the regime of the upper Danube River, below Belgrade, is also of that type. The contributions by the Tisza and Sava rivers, whose regimes are rather of a rainfall type, cause a shift in the hydrological regime. The Iron Gates reservoirs, which increase the water residence time by only about 6 days, have a minor effect on water flow at the scale of the annual cycle.

Besides data of rainfall, potential evapotranspiration and air temperature, which are forcing functions of the HYDROSTRAHLER model, additional constraints on the ecological RIVE model are the seasonal variations of water temperature, photoperiod and light intensity, represented by sine functions. During the photoperiod, the hourly irradiance is also calculated as a sine function (Billen *et al.*, 1994).

Lithology, land use and urban activity in the Danube basin

Diffuse sources of nutrients as estimated from lithology and land use

Soil–water interactions within the watershed determine the magnitude of diffuse sources of the nutrients, silica, nitrogen and phosphorus. The lithology alone determines the silica content of the surface and groundwater, while landcover and agricultural practices are important in determining nitrogen and, to a lesser extent, phosphorus concentrations.

More than one-third of the Danube watershed is covered by large loess formations, which, together

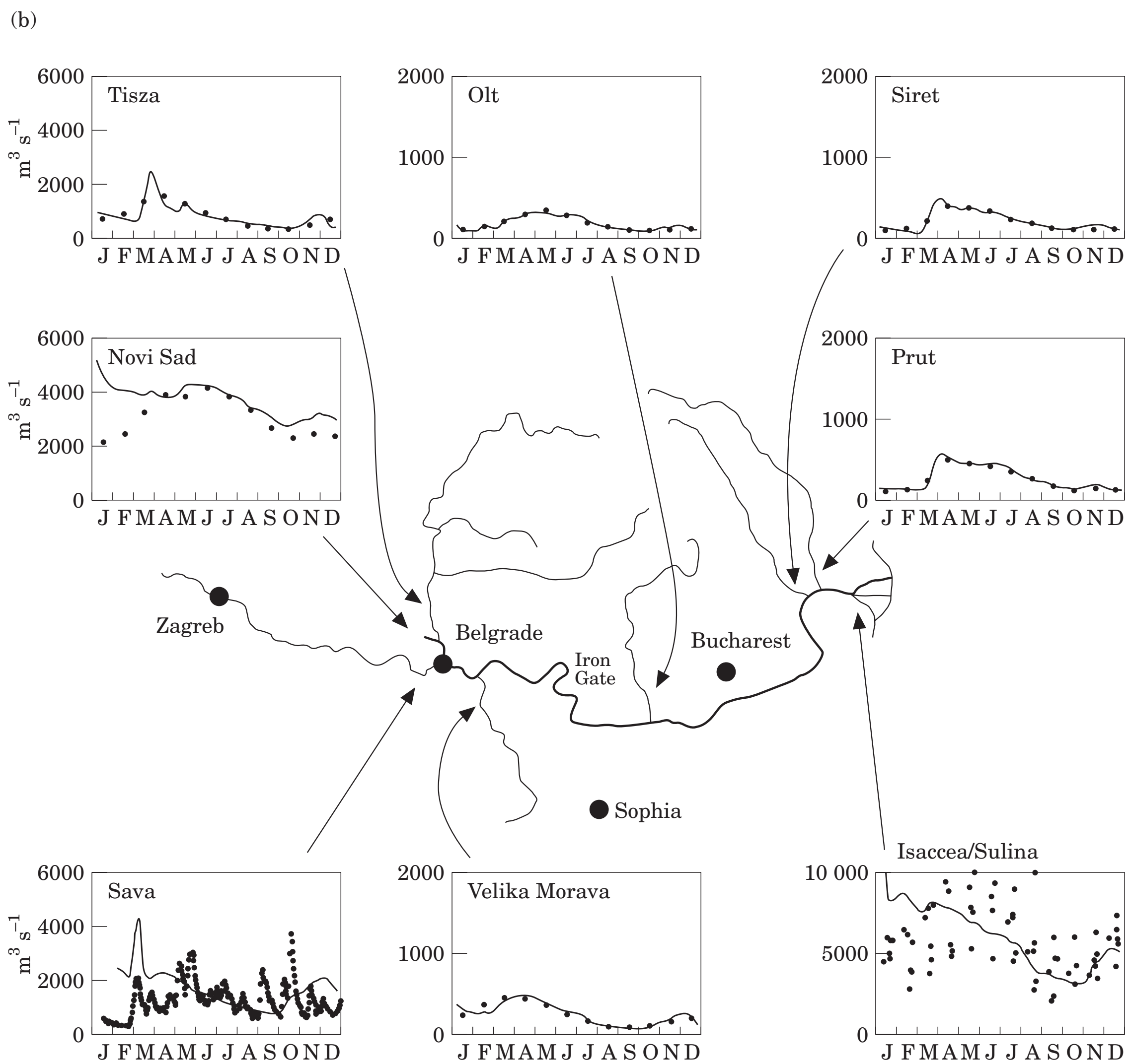

FIGURE 5. (b).

FIGURE 5. (a) Upper and (b) lower course of the Danube River. Simulation by the HYDROSTRAHLER model of seasonal variations of water discharges at the outlet of the sub-basins of the Danube River.

with recent alluvia, form the rich agricultural soil of the Hungarian, Romanian and Bessarabian plains. Flysch (detritic rock made of interbedded layers of shale and sandstone with carbonate cement, formed during the early Alpine and Carpathian orogenesis) covers another third of the watershed area. The Inn and Sava basins contain mostly secondary limestone, while magmatic rocks are found in the highest parts of the mountain ranges (Figure 6). A given silica concentration was assigned to each of these rock types on the basis of the compilation by Meybeck (1986). A mean silica concentration was thus calculated in the headwaters of each sub-basin based on the distribution of each lithological type in its catchment (Table 1).

A similar approach was followed for nitrogen and phosphorus by considering the geographical distribution of land-use types. Arable land occupies large areas in the middle of the basin and represents nearly half of the total watershed area. Large forests exist in the south-western part of the basin, as well as in the Transylvanian Alp and Carpathian regions. Grassland dominates the landscape in the lower parts of the mountain massifs (Figure 7). A mean nitrate and ortho-phosphate concentration in the headwaters was assigned to each of these three land-use types, and hence to each sub-basin, on the basis of the compilation by Howarth *et al.* (1996) and Billen and Garnier (1999), and taking into account the intensity of nitrogen fertilization (Table 2). In order to take into

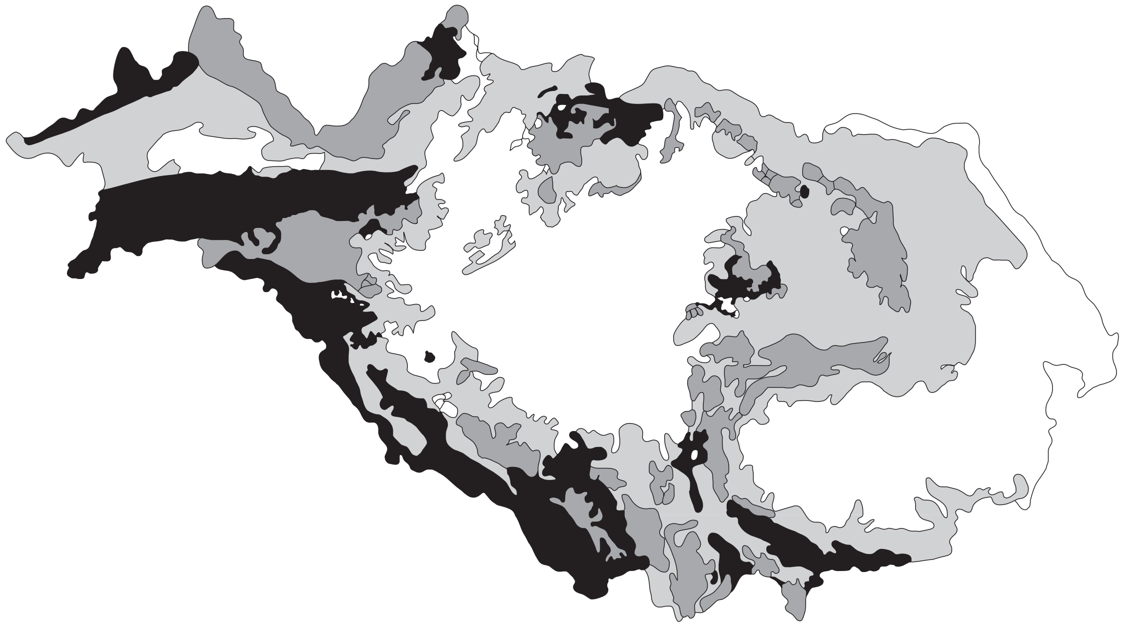

FIGURE 6. Map of the main lithological characteristics in the Danube basin (simplified from the Atlas of the Danubian Countries, 1989). (□) Loess and alluvions; (□) flysch; (■) secondary limestone; (▩) magmatic rocks.

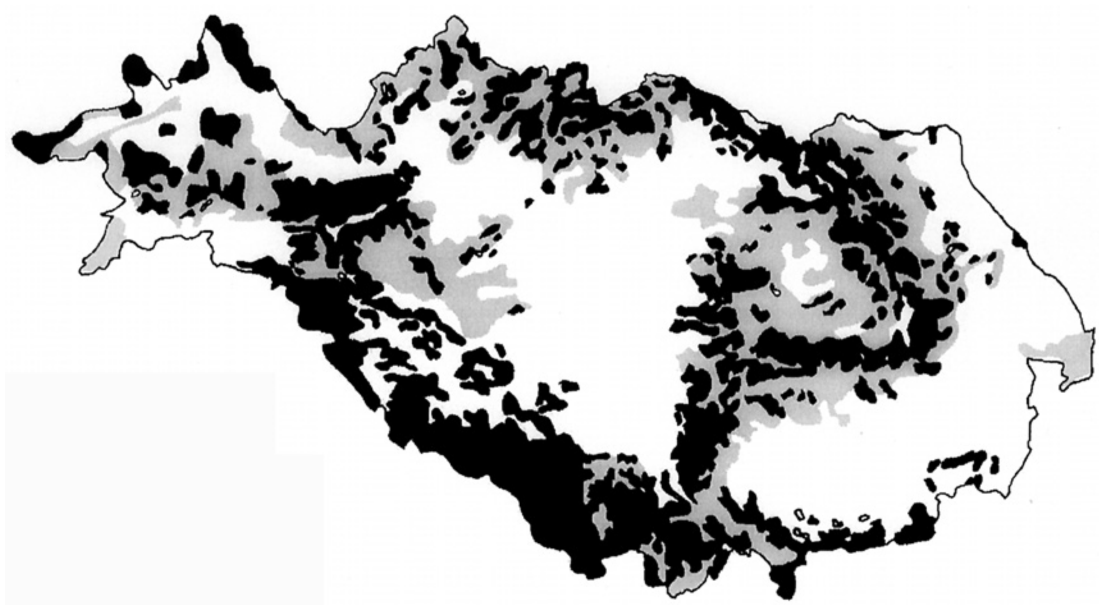

FIGURE 7. Map of arable land and forests in the Danube basin (simplified from the Atlas of the Danubian Countries, 1989). (■) Forest; (□) grassland; (□) arable land.

account the nutrient retention capacity of large alluvial plains, a riparian transfer factor of 0·5 was included for the direct watershed of the main branch of the Danube, according to the approach developed by Billen and Garnier (1999) for the Seine River system. By combining these estimates with the results of the hydrological model described above, diffuse sources of nutrients can be evaluated in the different sub-basins for the hydrological reference conditions of the years 1988–1991 (Table 3).

Point sources of nitrogen and phosphorus

In contrast to silica, which originates only from the weathering of rocks and therefore only has diffuse

TABLE 1. Distribution of lithological units among the sub-basins of the Danube River system, and estimated silica concentration in headwaters

Sub-basin	Total area (km^2)	Loess and alluvium (%)	Flysch[a] (%)	Secondary limestone[a] (%)	Magmatic rocks (%)	SiO_2 (μM)
Upper Danube	49 600	7	52	22	19	75
Inn	26 100	18	8	70	4	70
Morava	26 600	20	34	11	34	95
Drava	40 200	39	14	13	34	105
U-Danube DC	112 500	50	24	12	13	89
Sava	95 700	14	32	45	9	71
Velika Morava	37 400	1	39	21	39	92
Tisa	157 200	48	36	3	12	86
Olt	24 000	26	48	0	26	89
Siret	44 000	26	68	0	6	69
Prut	28 400	50	50	0	0	75
D-Danube DC	175 300	68	19	12	8	97

U-Danube DC=Upper Danube direct catchment from its junction with the Inn River to Novi Sad; D-Danube DC=Lower Danube direct catchment from Novi Sad to the mouth.
[a]Headwater concentration of SiO_2 in the different lithological units (Meybeck, 1986).
Loess and alluvium=100 μM, flysch =50 μM, secondary limestone=60 μM, magmatic rocks=150 μM.

TABLE 2. Distribution of land use in the sub-basins of the Danube River system, and estimated mean nitrate concentrations in headwaters

Sub-basin	Total area (km^2)	Forest[a] (%)	Grassland[a] (%)	Arable land[a] (%)	Riparian transfer coefficient	NO_3 (μM)
Upper Danube	49 600	32	15	53	1	384·9
Inn	26 100	14	64	22	1	188·8
Morava	26 600	27	50	23	1	191·4
Drava	40 200	22	50	28	1	225·4
U-Danube DC	112 500	19	29	52	0·5	200·3
Sava	95 700	59	16	25	1	194·8
Velika Morava	37 400	48	40	12	1	113·6
Tisza	157 200	17	37	46	1	343·9
Olt	24 000	29	54	17	1	151·8
Siret	44 000	31	46	23	1	190·2
Prut	28 400	14	20	66	1	474·8
D-Danube DC	173 300	15	18	67	0·5	246·5
Total	817 000	26	30	44	1	

U-Danube DC=Upper Danube direct catchment from its junction with the Inn River to Novi Sad; D-Danube DC=Lower Danube direct catchment from Novi Sad to the mouth.
[a]Headwater concentration of NO_3 in the different land-use types: forest=20 μM, grassland=50 μM, arable land=700 μM.

sources, significant amounts of nitrogen and phosphorus are added to the river system as point sources of wastewater.

A detailed census of domestic and industrial nutrient inputs to surface water was carried out in the late 1980s by Guilbot *et al.* (1993) and Marcel and Soulié (1992) for the European Bank for Reconstruction and Development. We have used this information to assess point sources of organic carbon, nitrogen and phosphorus. Domestic sources are based on the population census, using specific per capita loads of 20 g organic C day^{-1}, 14 gN day^{-1} and 3·5 gP day^{-1} (WHO, 1982; de Cuyper & Loutz, 1992; Billen *et al.*, 1999; Servais *et al.*, 1999). The evaluation of industrial loading is based on a census of workers in the main industrial sectors and the corresponding specific

TABLE 3. Estimates of non-point sources of nutrients in the sub-basins of the Danube River system for the conditions of reference years 1988–1991

Sub-basin	Basin area (km^2)	Specific disch ($l\ km^{-2}\ s^{-1}$)	Non-point sources ($kgN\ km^{-2}\ day^{-1}$)	($kgP\ km^{-2}\ day^{-1}$)	($kgSi\ km^{-2}\ day^{-1}$)	($kgTN\ yr^{-1}$)	($kTP\ yr^{-1}$)	($kgTSi\ yr^{-1}$)
Upper Danube	49 600	13·4	6·38	0·04	2·48	113·9	0·7	44·3
Inn	26 100	28·7	4·02	0·15	4·9	37·8	1·4	46·0
Morava	26 600	5·05	1·17	0·03	1·17	11·2	0·3	11·2
Drava	40 200	15	3·49	0·09	3·52	50·5	1·3	50·9
U-Danube DC	112 500	5	0·60	0·07	1·07	24·5	2·7	43·5
Sava	95 700	19·85	3·89	0·3	3·17	134·0	10·3	109·2
Tisza	157 200	5·2	1·15	0·035	1·16	65·1	2·0	65·6
Velika Morava	37 400	6·48	1·7	0·26	1	22·9	3·5	13·5
Olt	24 000	7·1	1·25	0·075	1·52	10·8	0·6	13·1
Siret	44 000	4·92	1·12	0·03	0·81	17·7	0·5	12·8
Prut	28 400	9·37	5·44	0·089	1·71	55·6	0·9	17·5
D-Danube	175 300	5	0·74	0·07	1·17	46·9	4·2	74·0
Total	817 000	7·49				591·0	28·5	501·7

U-Danube DC=Upper Danube direct catchment from its junction with the Inn River to Novi Sad; D-Danube DC= Lower Danube direct catchment from Novi Sad to the mouth.

TABLE 4. Specific emission coefficients by worker-day, established for the major industrial sectors in East European countries for the 1980s (Guilbot *et al.*, 1993)

	East European countries				
Industrial sector	C (g worker^{-1} day^{-1})	N (g worker^{-1} day^{-1})	P (g worker^{-1} day^{-1})	Inhabitant equivalent	Western Europe*
Metallurgy	30	0	0	1·5	
Chemistry	2600	500	100	130	500
Paper industry	40 000	0·2	0·1	2000	430
Textile industry	320	4	2	16	
Food industry	100	35	10	5	150

*When available, corresponding values calculated for West European countries from coefficients adopted by French Water Authorities (Billen *et al.*, 1999) are given for comparison.

TABLE 5. Estimated domestic and industrial loads in the sub-basins of the Danube River system

Sub-basin	Basin area (km^2)	Actual population	Industrial load (inhabitant equiv.)	Density (inhabitant equiv. km^{-2})	Input N (kgTN yr^{-1})	Input P (kgTP yr^{-1})	N/P ratio (w/w)
Upper Danube	49 600	1 522 145	0	31	5·5	1·9	2·9
Inn	26 100	893 515	24 300	35	3·3	1·2	2·9
Morava	26 600	3 545 340	1 600 000	193	23·5	5·5	4·3
Drava	40 200	3 297 045	593 000	97	15·9	4·6	3·5
U-Danube DC	112 500	15 847 285	7 130 000	204	97·8	24·8	3·9
Sava	95 700	9 318 595	0	97	33·5	11·7	2·9
Tisza	157 200	14 176 780	15 372 000	188	126·1	28·9	4·4
Velika Morava	37 400	4 015 880	0	107	14·5	5·1	2·9
Olt	24 000	2 162 215	4 078 000	260	27·4	5·7	4·8
Siret	44 000	4 003 970	0	91	8·8	3·1	2·9
Prut	28 400	2 931 490	6 106 000	318	37·9	8·1	4·7
D-Danube DC	175 300	16 008 200	39 259 000	315	271·6	48·6	5·6
Total	817 000	77 722 460	74 161 000	186	665·9	149·0	4·5

U-Danube DC=Upper Danube direct catchment from its junction with the Inn River to Novi Sad; D-Danube DC=Lower Danube direct catchment from Novi Sad to the mouth.

pollution coefficients established for the technological processes in use in ‘ Eastern countries ’ in the 1980s (Table 4). As the effect of wastewater treatment facilities on total N and P release at the scale of the whole Danube catchment was probably limited during this period, it was completely neglected (Table 5).

The mean equivalent population density of the whole Danube catchment area (184 inhabitant equivalents km^{-2}) is as high as that of most West European Atlantic river basins. Even higher densities are found along the lower course of the main Danube branch and in the Prut sub-basin, while they are much lower in predominantly mountainous sub-basins such as the Upper Danube, Inn and Siret basins (Table 5).

Transfer and retention of nutrients in the Danube drainage network

Modelling the biogeochemical functioning in the Danube River

The model of ecological functioning (RIVE model, Billen, *et al.*, 1994; Garnier *et al.*, 1995) constitutes the common module for the calculation of water quality in the sub-basins and the main branch of the Danube River. It consists of 22 variables, including nutrients (nitrate and ammonium, phosphate, dissolved silica), dissolved and particulate organic matter (as two classes of biodegradability), two taxonomic groups of phytoplankton (diatoms and non-diatoms), two groups of zooplankton (rotifers and

TABLE 6. Kinetic formulation of the processes taken into account in the RIVE model, and values of the corresponding parameters

Process	Kinetic expression	Parameters	Meaning	Diatoms	Chloro-phyc.	Units
Phytoplankton dynamics						
Photosynthesis (photo)	kmax (1-exp-(α I/kmax)) PHY	kmax[a]	maximal rate of photosynth.	0·2	0·5	h^{-1}
		α	initial slope of P/I curve	0·0012	0·0012	h^{-1}/(μE.m^{-2} s^{-1})
Reserve synthesis	srmax *M*(S/PHY,Ks) PHY	srmax[a]	max. rate of reserve synthesis	0·15	0·37	h^{-1}
		Ks	1/2 saturation est	0·06	0·06	
Reserve catabolism	ker R	ker.[a]	rate of R catabolism	0·2	0 2	h^{-1}
Growth (phygrwth)	mufmax *M*(S/PHY,Ks) lf PHY	mufmax	max. growth rate[a]	0·07	0·14	h^{-1}
Nutrient limitation factor	with lf=*M*(PO_4,Kpp)	Kpp	1/2 sat. cst for P uptake	15	46	μg P l^{-1}
	or *M*(NO_3+NH_4, Kpn)	Kpn	1/2 sat. cst for N uptake	70	70	μg N l^{-1}
	or *M*(SiO_2, KpSi)	KpSi	1/2 sat. cst for Si uptake	0·42	—	mgSiO_2 l^{-1}
Respiration	maint PHY+ecbs phygrwth	maint[a]	maintenance coefficient	0·002	0·002	h^{-1}
		ecbs	energetic cost of biosynthesis	0·5	0·5	—
Excretion (phyex)	exp photo+exb PHY	exp	' income tax ' excretion	0·0006	0·0006	h^{-1}
		exb	' property tax ' excretion	0·001	0·001	h^{-1}
Lysis (phylys)	kdf+kdf (1+vf)	kdf[a]	mortality rate	0·004	0·004	h^{-1}
		vf[+]	parasitic lysis factor	0/20	0/20	—
Phyto sedimentation	(vsphy/depth).PHY	vsphy	sinking rate	0·004	0·0005	m h^{-1}
NH_4 uptake	phygrwth/cn NH_4/NH_4+NO_3)	cn	algal C/N ratio	7	7	g C (g N)$^{-1}$
NO_3 uptake	phygrwth/cn NO_3/(NH_4+NO_3)					
PO_4 uptake	phygrwth/cp	cp	algal C/P ratio	40	40	g C (g P)$^{-1}$
SiO_2 uptake	phygrwth/cSi	cSi	algal C/Si ratio	2	—	g C (g SiO_2)$^{-1}$
Temperature dependency	p(T)=p(Topt).exp(-(T-Topt)^2/dti^2)	Topt	optimal temperature	18	35	°C
		dti	range of temperature	13	17	°C
Zooplankton dynamics				Total zooplankton		
Zoo growth (zoogwth)	μzox.*M*(PHY-PHYo),KPHY).ZOO	μzox	max. growth rate	0·02[a]		h^{-1}
		KPHY	1/2 sat cst to PHY	0·4		mgC l^{-1}
		PHYo	threshold phyto conc.	0·1		mgC l^{-1}
Zoo grazing	grmx.*M*((PHY-PHYo)KPHY).ZOO	grmx	max. grazing rate	0·035[a]		h^{-1}
Zoo mortality	kdz.ZOO	kdz	mortality rate	0·001[a]		h^{-1}
Temperature dependency	p(T)=p(Topt).exp(-(T-Topt)^2/dti^2)	Topt	optimal temperature	22		°C
		dti	range of temperature	12		°C
Lamellibranchs				Dreissena		
Filtration rate		fmax	max. filtration rate	0·01[a]		m^3gDW^{-1}h^{-1}
Temperature dependency	p(T)=p(Topt).exp(-(T-Topt)^2/dti^2)	Topt	optimal temperature	25		°C
		dti	range of temperature	8		°C
Bacterioplankton dynamics				Small bact.	Large bact.	
HPi production by lysis	εpi. (phylys+bactlys+zoomort)	εpl	HP1 fraction in lysis pdcts	0·2		—
		εp2	HP2 fraction in lysis pdcts	0·2		—
		εp3	HP3 fraction in lysis pdcts	0·1		—
Enzyme HPi hydrolysis	kib.HPi	k1b	HP1 lysis rate	0·005		h^{-1}
		k2b	HP2 lysis rate	0·00025		h^{-1}

TABLE 6. *Continued*

Process	Kinetic expression	Parameters				
			Meaning	Diatoms	Chloro-phyc.	Units
HPi sedimentation	(vsm/depth).Hip	Vs	Hip sinking rate	0·05		$m\ h^{1}$
Hid production by lysis	δe.(phylys+bactlys+zoomort)	εd1	HD1 fraction in lysis pdcts	0·2		—
		εd2	HD2 fraction in lysis pdcts	0·2		—
		εd3	HD3 fraction in lysis pdcts	0·1		—
Enzyme HDi hydrolysis	eimax. *M*(HDiKHi).BAC	e1max	max. rate of HD1 hydrolysis	0·75	0·75	h^{-1}
		e2max	max. rate of HD2 hydrolysis	0·25	0·25	h^{-1}
		KH1	1/2 sat cst for HD1 hydrol.	0·25	0·25	$mgC\ l^{-1}$
		KH2	1/2 sat cst for HD1 hydrol.	2·5	2·5	$mgC\ l^{-1}$
Direct substrate uptake	bmax. *M*(S,Ks).BAC	bmax	max. S uptake rate	0·2	0·8	h^{-1}
		Ks	1/2 sat cst for S uptake	0·1	0·1	$mgC\ l^{-1}$
Bact. growth (bgwth)	Y. bmax. *M*(S,Ks). BAC	Y	growth yield	0·25	0·25	—
Bact. mortality (bactlys)	kdb.BAC	kdb	bac. lysis rate	0·01	0·01	h^{-1}
Bact. sedimentation	(vsb/depth).BAC	vsb	bacteria sinking rate	0	0·01	$m\ h^{-1}$
Ammonification	(1-Y(/Y.bgwth/cn	cn	bact. C:N ratio		7	gC/gN
PO_4 production	(1-Y)/Y.bgwth/cp	cp	bact. C:P ratio		40	gC/gP
Temperature dependency	$p(T)=p(Topt).exp(-(T-Topt)^2/dti^2)$	Topt	optimal temperature	25	25	°C
		dti	range of temperature	15	15	°C
Nitrification and phosphorus dynamics				Nitrifying bacteria		
NIT growth (nitgwth)	$\mu nix.M(NH_4,KNH_4).M(O_2,KO_2)$. NIT	μnix[a]	max. growth rate of NIT	0·05		h^{-1}
		KNH_4	1/2 sat cst for NH_4	7		$mgN\ l^{-1}$
		KO_2	1/2 sat cst for O_2	0·6		$mgO_2\ l^{-1}$
NH_4 oxidation	nitgwth/rdnit	rdtnit	NIT growth yield NIT	0·1		mgC/mg NH_4
NIT mortality	kdnit.NIT	kdnit[a]	NIT mortality rate	0·01		h^{-1}
PO_4 adsorpt/desorpt.	Langmuir isotherm	Pac	SM max. adsorpt. capacity	0·0045		mgP/mgMES
(planktonic phase)		KPads	1/2 saturation ads. cst	0·3		$mgP\ l^{-1}$
Temperature dependency	$p(T)=p(Topt).exp(-(T-Topt)^2/dti^2)$	Topt	optimal temperature	23		°C
		dti	range of temperature	16		°C
Benthos recycling						
Susp. matter sedim.	(vsm/depth)*MES	vsm	sinking rate			$m\ h^{-1}$
Diffusion (interstitial ph.)	Fick law	Di	app. diffusion coefficient	2×10^{-5}		$cm^2\ s^{-1}$
Mixing (solid phase)	Fick law	Ds	mixing coefficient	2×10^{-6}		$cm^2\ s^{-1}$
OrgN mineralis. (maorg)	kib.HPi/cn					
OrgP mineralis.	kip.HPi/cp	k1p[a]	orgP hydrolysis rate of HP1	0·05[a]		h^{-1}
		k2p[a]	orgP hydrolysis rate of HP2	0·0025[a]		h^{-1}
Benth. nitrification	$kNi*NH_4$ (in oxic layer)	kNi	1st order nitrification cst	1		h^{-1}
NH_4 adsorpt/desorpt.	1st order equilibrium	Kam	1st order adsorpt. cst for NH_4	30		—
PO_4 adsorpt/desorpt.	1st order equilibrium	Kpa	PO_4 adsorpt. (oxic layer)	35		—
(in benthos)		Kpe	PO_4 adsorpt. (anoxic layer)	1·7		—
SiO^2 redissolution	kdbSi.SIB	kdbSi	silica redissolution rate	0·01		h^{-1}
Temperature dependency	$p(T)=p(Topt).exp(-(T-Topt)^2/dti^2)$	Topt	optimal temperature25			°C
		dti	range of temperature	20		°C

[a]These parameters depend on temperature according to the relation mentioned.
+*M*(C,Kc)=C/(C+Kc): hyperbolic Michaelis–Menten function.
+vf: parasitic lysis amplification function. It is maintained at zero while algal density of each group remains lower than a threshold value of 65 μg Chl*a* l^{-1} and temperature is below 15 °C.

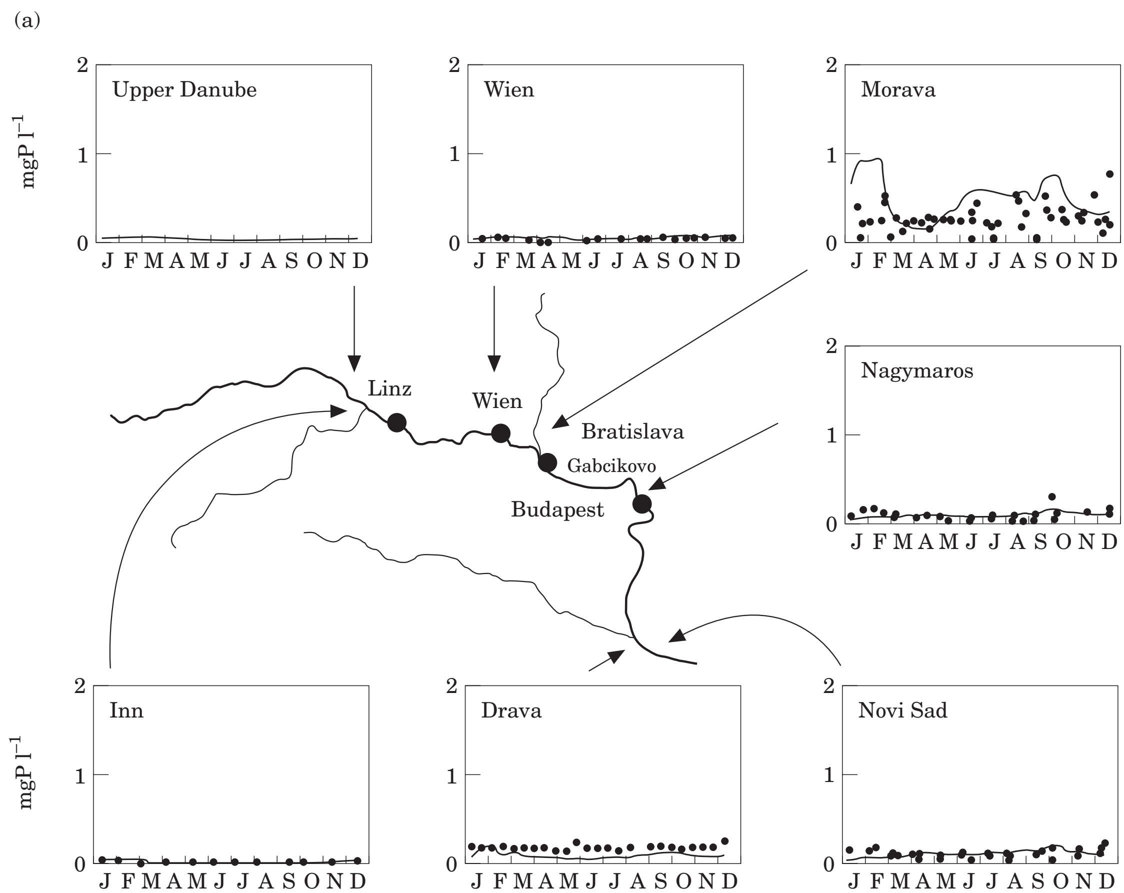

FIGURE 8. (a). *Continued on p. 299.*

microcrustaceans) and bacteria. The description of the phytoplankton dynamics is based on the formulation by Lancelot *et al.* (1991), which distinguishes between photosynthesis—controlled by light intensity—and algal growth—controlled by nutrient availability. The module has been adapted to two groups of algae (diatoms and non-siliceous algae), and a formulation for loss processes by excretion and grazing has been added (Garnier & Billen, 1993; Garnier *et al.*, 1998). The degradation of organic matter and bacterioplankton dynamics are described according to Billen (1991). The model also includes a calculation of nutrient exchanges across the sediment–water interface as a result of a given sedimentation flux of organic material, taking into account organic matter degradation, associated ammonium and phosphate release, oxygen consumption, nitrification and denitrification, phosphate and ammonium adsorption onto inorganic material, mixing processes in the interstitial and solid phases, and accretion of the sedimentary column by inorganic matter sedimentation. Sedimented biogenic silica is re-dissolved according to first-order kinetics. Water-column nitrification (Brion & Billen, 1998) and phosphate adsorption on suspended inorganic particles (and their subsequent sedimentation) are also taken into account in the model.

The kinetics of the major processes involved in the ecological functioning and the corresponding parameters are mostly derived from experimental field work (Garnier *et al.*, 1998). Essentially, the same kinetic formulations were used in the model applied to the Danube River as in the original description of the RIVERSTRAHLER model. Only the parameter values were occasionally modified within the narrow range of experimental determinations (Table 6).

Validation of the biogeochemical model

To validate the model, the calculations are compared with observed data of water quality (nutrients: N, P and Si, and phytoplankton: Chl *a*) at the outlet of each sub-basin, and at reasonable intervals along the main axis. We generally used data collected at the Bucharest Convention project during the period 1988–1991, which was used as the reference period.

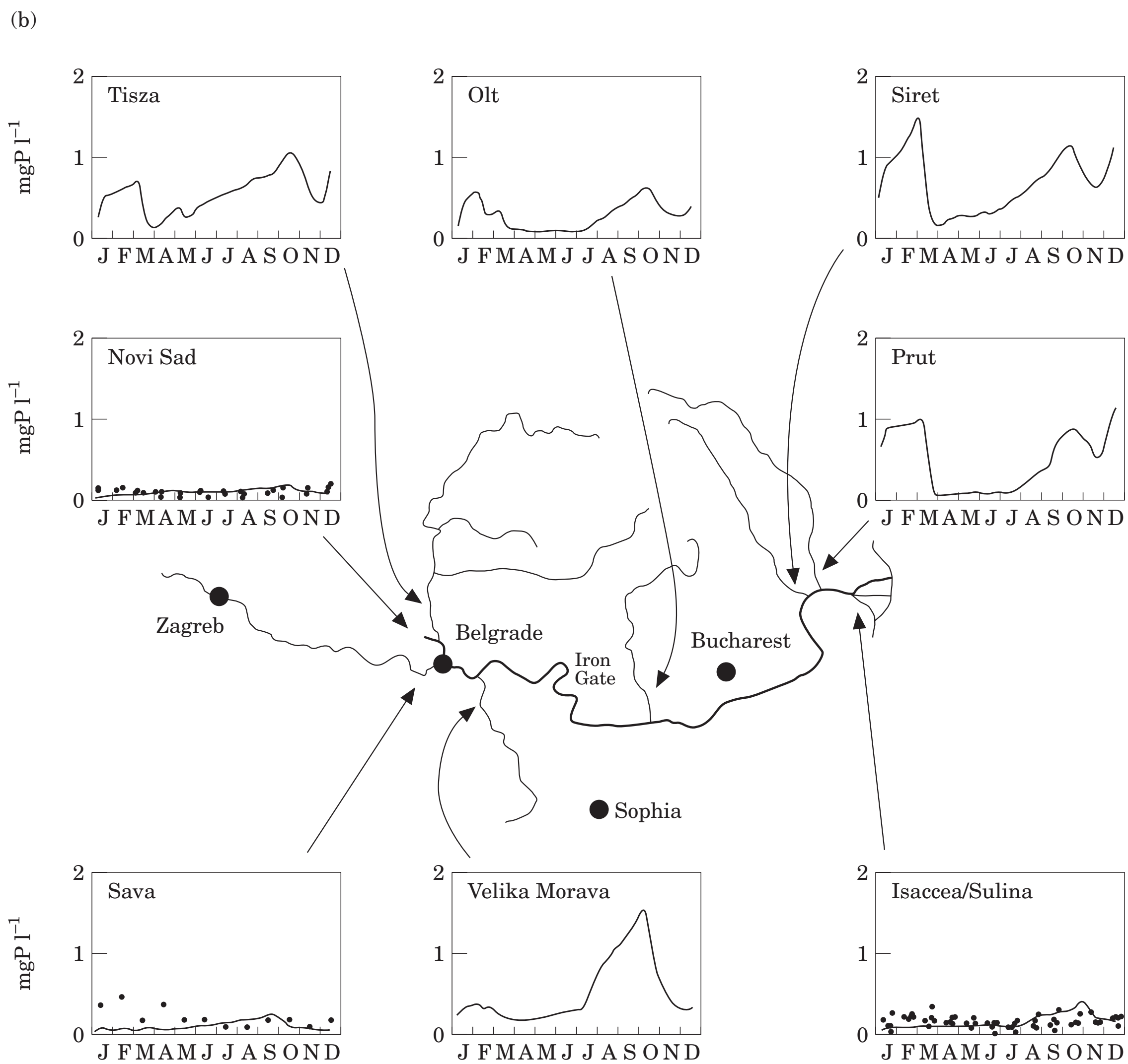

FIGURE 8 (b).

FIGURE 8. (a) Upper and (b) lower course of the Danube River. Simulation by the RIVERSTRAHLER model of seasonal phosphate variations for the period 1988–1990. Experimental data for the same period are given for comparison.

This data set was complemented by published data (Hammer & Mac Kichan, 1981; Kiss *et al*., 1988 in Tamas-Dvihally, 1993; Aponasenko *et al*., 1991 Lyons *et al*., 1992; Chernyavaskaya *et al*., 1993; Cociasu *et al*., 1997). The resulting database remains rather incomplete, particularly for silica and phytoplankton.

As far as can be judged from these validation data, the model reasonably reproduces the values of most variables tested (Figures 8–11).

Although phosphate concentrations are rather high in most of the downstream tributaries, they are, surprisingly, maintained at the level of 0·2 mg P-PO_4 l^{-1} at the mouth of the delta (Isaccea/Sulina station, Figure 8); this value is lower than that of several Western European rivers (0·5 and 0·3 mg P-PO_4 l^{-1} for the French Seine and Loire rivers, respectively, 0·5 mg P-PO_4 l^{-1} for the Scheldt in Belgium and 0·12 mg P-PO_4 l^{-1} for the Rhine), and may be due to strong dilution by phosphate-poor upstream water (the flow at Vienna represents one-third of the total flow at the delta), but also to high retention/uptake in the drainage network (see below). Nitrate concentrations of up to 5 mgN l^{-1} are typical values for intensively agricultural watersheds (Figure 9). Variations in silica levels between sub-basins only depend

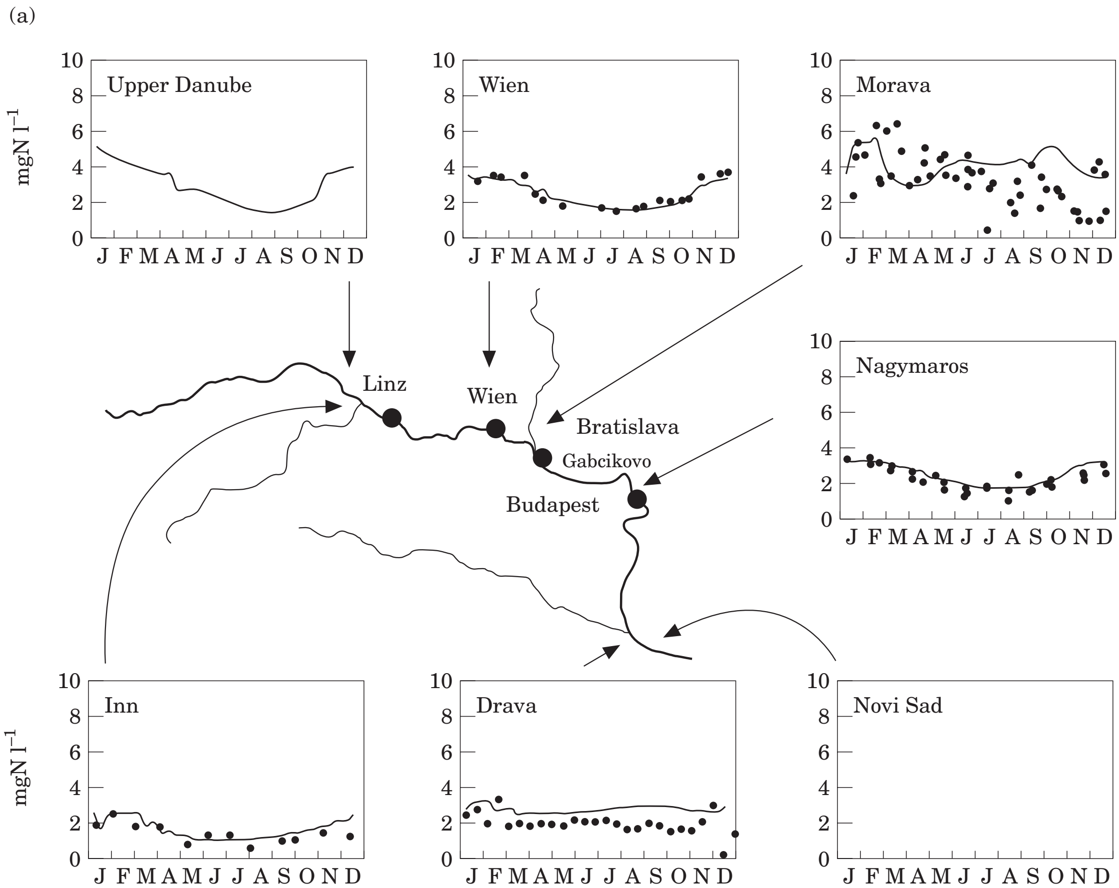

FIGURE 9. (a). *Continued on p. 301.*

on the lithology, and the uptake by diatoms causes seasonal variations (Figures 10 and 11). Large seasonal variations in silica concentrations are generally related to eutrophication (Conley *et al.*, 1993; Garnier *et al.*, 1995; Conley, 1997; Humborg *et al.*, 1997). As can be expected from the inputs of N and P by point sources, all the affluents of the left bank (Morava, Tisza, Olt, Siret and Prut) appear to be eutrophic.

Nutrient budget and retention in the hydrographic network of the Danube

The fluxes of nutrients in the Black Sea calculated by the RIVERSTRAHLER model for the chosen reference period are in the same range as those obtained with the experimental database of nutrient concentrations and flow values (Cociasu *et al.*, 1997), or calculated in the framework of the EC Phare programme (Masaryk & Varley, 1997) (Table 7). Our estimates are within 15% of data gathered by Cociasu *et al.* (1997). A greater discrepancy is found for total nitrogen delivery compared to the Phare programme estimate, obtained by the sum of the input/output in each country (Table 7). The retention in the drainage network calculated by the model is about 30% of gross inputs for nitrogen and silica, and up to 70% for phosphorus.

The relationship between nitrate riverine delivery and human population density found by Peierls *et al.* (1991) for nitrogen in the major rivers of the world was applied to a number of European rivers for both N and P delivery: the Danube fluxes compare well with those of other European river systems (Figure 12). This shows that a higher population density results in increasing inputs from both point sources (increased wastewater input) and non-point sources (increased fertilizer inputs). As demonstrated by the hypothetical scenarios proposed by Billen and Garnier (1997), a shift from P to N limitation (a decreasing N/P ratio) occurs with increasing population density (Figure 12). Indeed, the N/P ratio in the outflow of the Danube River suggests that it may cause phosphorus, rather than nitrogen, limitation of phytoplankton in the coastal zone of the Black Sea. On the

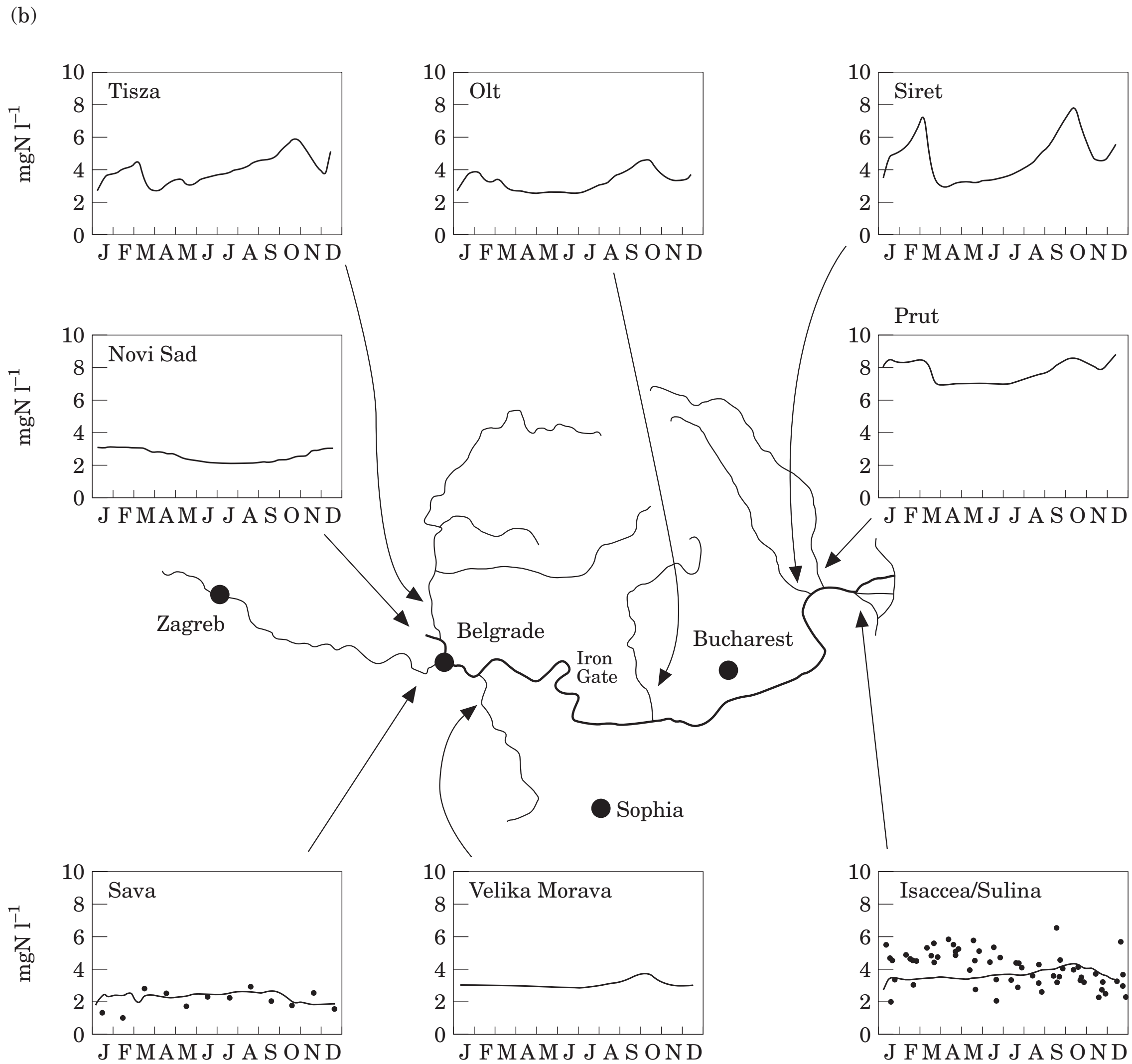

FIGURE 9 (b).

FIGURE 9. (a) Upper and (b) lower course of the Danube River. Simulation by the RIVERSTRAHLER model of the seasonal nitrate variations for the period 1988–1990 (ammonium in dotted line · · ·). Experimental data for the same period are given for comparison.

other hand, the Si/P ratio of 7(w/w), about half the value reported for actively growing diatoms (13·5 w/w, Conley *et al.*, 1989) indicates a severe silicate depletion in the riverine delivery.

Regarding silica, the assumption that the Iron Gates reservoirs play a major role as nutrient retention sites has recently been discussed by Humborg *et al.* (1997). In order to test this hypothesis, a simulation was run with the morphology of the Danube River as it was before the construction of the Iron Gates reservoirs in 1970. The results do not show a significantly lower retention of silica. Diverging from that of Humborg *et al.* (1997), our result suggests that nutrient retention in the Danube River system does not occur predominantly within the Iron Gates, but is more evenly distributed throughout the drainage network. Moreover, our model suggests that silica retention within the drainage network is largely dependent on riverine eutrophication driven by phosphate inputs. Indeed, a scenario with a 90% abatement of the total point phosphorus load showed a considerable reduction in phytoplankton biomass (chlorophyll *a*) and much higher silica concentrations during the period of phytoplankton development, from April to October (Figure 13). Compared to the reference stimulation (Table 7), silica retention decreased from about 30% to less than 18% of gross inputs in this phosphate reduction scenario.

(a)

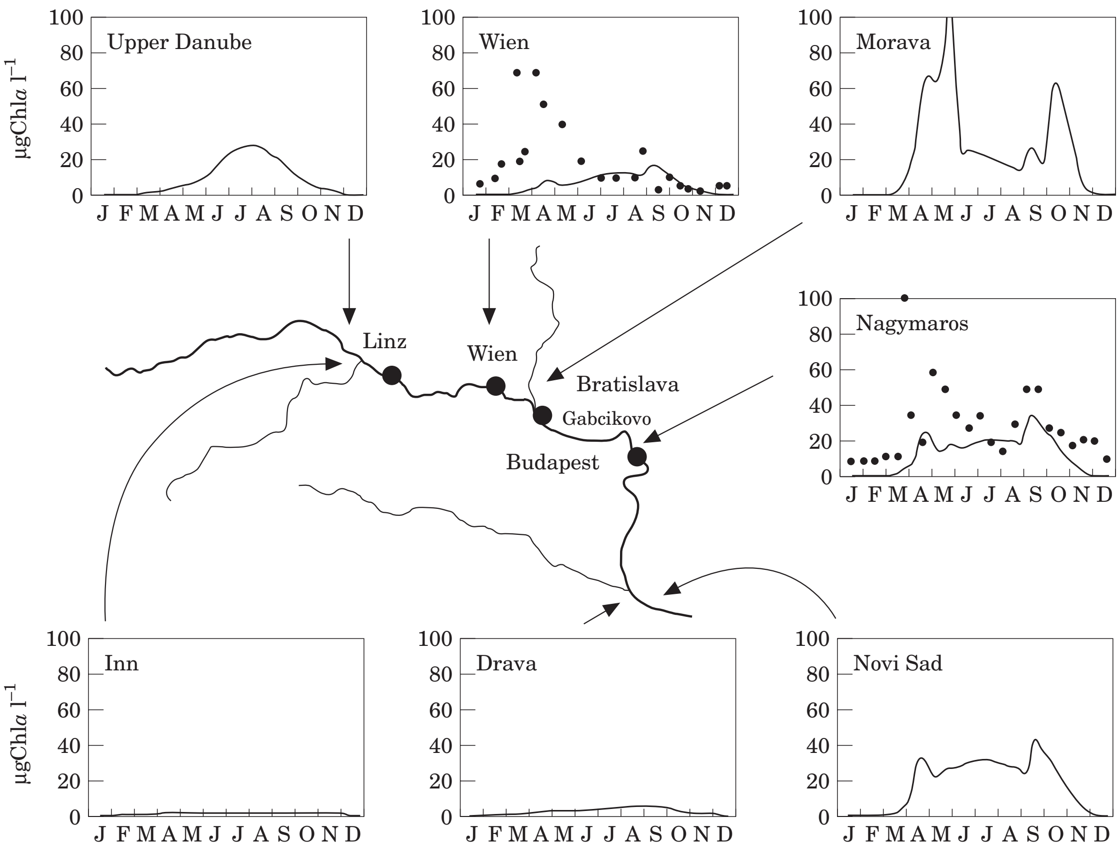

FIGURE 10. (a). *Continued on p. 303.*

TABLE 7. Calculated budget of nutrient input, transfer and delivery by the Danube River system for the reference period from 1988 to 1991

	$kgTN\ yr^{-1}$		$kgTP\ yr^{-1}$			
	Total N	NO_3+NH_4	Total P	PO_4	$kgTSi\ yr^{-1}$	Si/Total P (w/w)
Non-point sources						
Model calculations[a]	591		29		502	17·3
Phare estimates[b]	578		47		—	
Point sources						
Model calculations	666		149		0	
Phare estimates	416		83		—	
Output to the Black Sea						
Model calculations	936	858	51	24	357	7[d]
Phare estimates	447		46		—	—
Observed[c]	—	723	—	26	294	—
Percentage retention	%		%		%	
Model calculations	26		70		29	
Phare estimates	55		65		—	

[a]The model calculates the sum of all inorganic, organic, dissolved and particulate forms. [b]Phare programme estimates for 1998 and 1989.[c]Observed values from Cociasu's database (Cociasu *et al.*, 1996 and pers. comm.). [d]Si/P calculated with total phosphorus and PO_4. Compare with the ratio required for the growth of marine diatoms: 13·5 (Conley *et al.*, 1993).

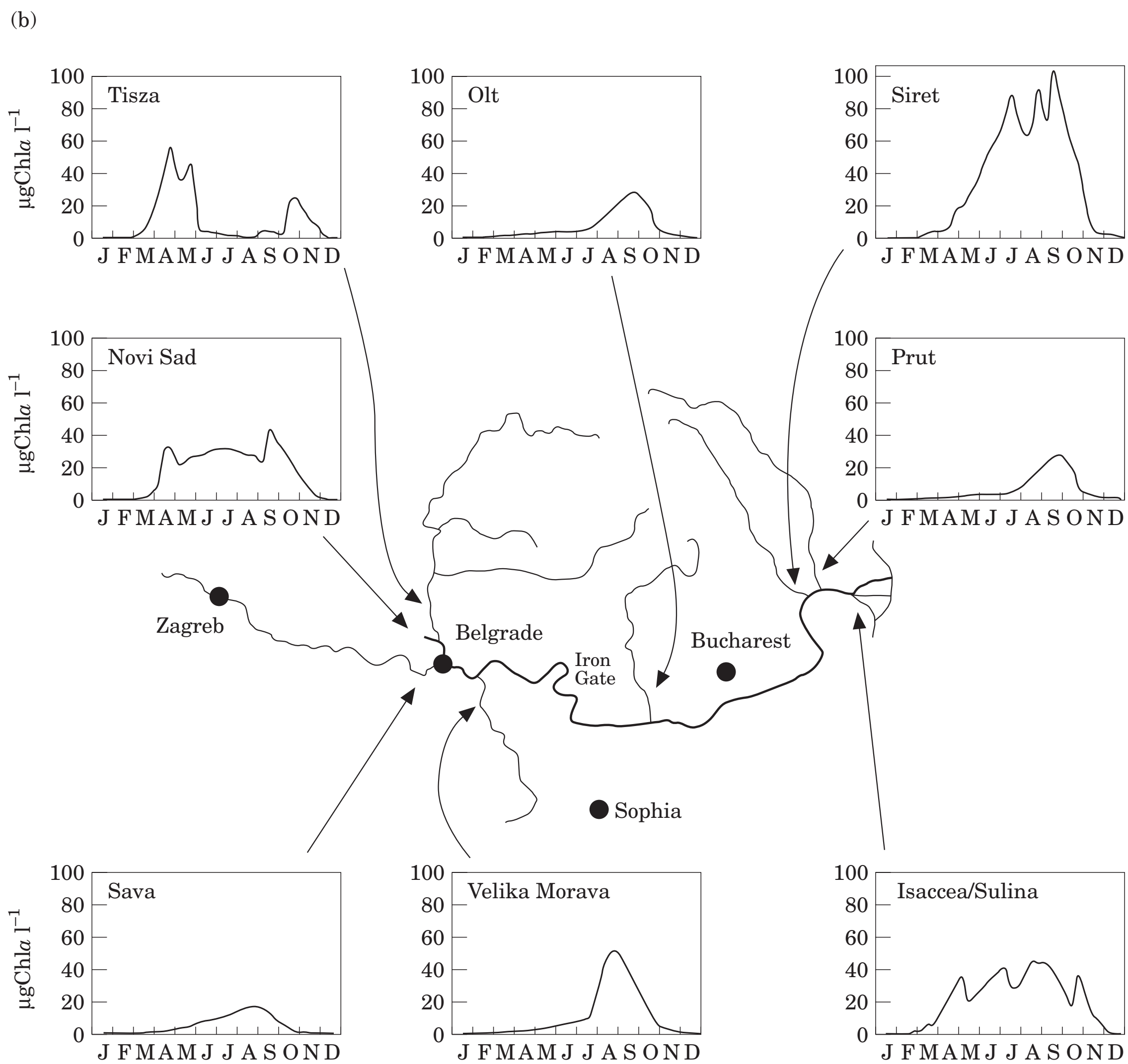

FIGURE 10. (b).

FIGURE 10. (a) Upper and (b) lower course of the Danube River. Simulation by the RIVERSTRAHLER model of the seasonal phytoplankton variations for the period 1988–1990. Experimental data for the same period are given for comparison.

Analysis of the past trends of nutrient delivery

Since the beginning of the 1990s, a sharp drop in the annual N and P delivery of the Danube to the Black Sea has been observed (Cociasu *et al.*, 1997) (Figure 14). Given the low interannual variability of mean water discharge, this drop clearly reflects a decrease in nutrient concentrations in Danube waters. This drop is concomitant with the sharp decline in economic activities from 1991 onwards (see Lemarchand & Le Guidec, 1997). During the same period, several signs of recovery of the Black Sea coastal ecosystem have been noticed (Lancelot *et al.*, 1998). Scenario simulations with the ecological BIOGEN model of the coastal Black Sea suggest that these changes are related to the reduction in nutrient delivery by the Danube River (Lancelot *et al.*, 2002). In order to verify whether the trends observed in the Danube nutrient delivery can indeed be explained by the documented modification of human activity in the watershed, we constructed a scenario to reproduce these new constraints.

The most significant change consists of a dramatic reduction in industrial activity. Overall indices of industrial production (in monetary value) have decreased by 30% in Hungary, 40% in Slovakia and 50% in Romania between 1989 and 1994 (Lemarchand & Le Guirec, 1997). Consequently, we

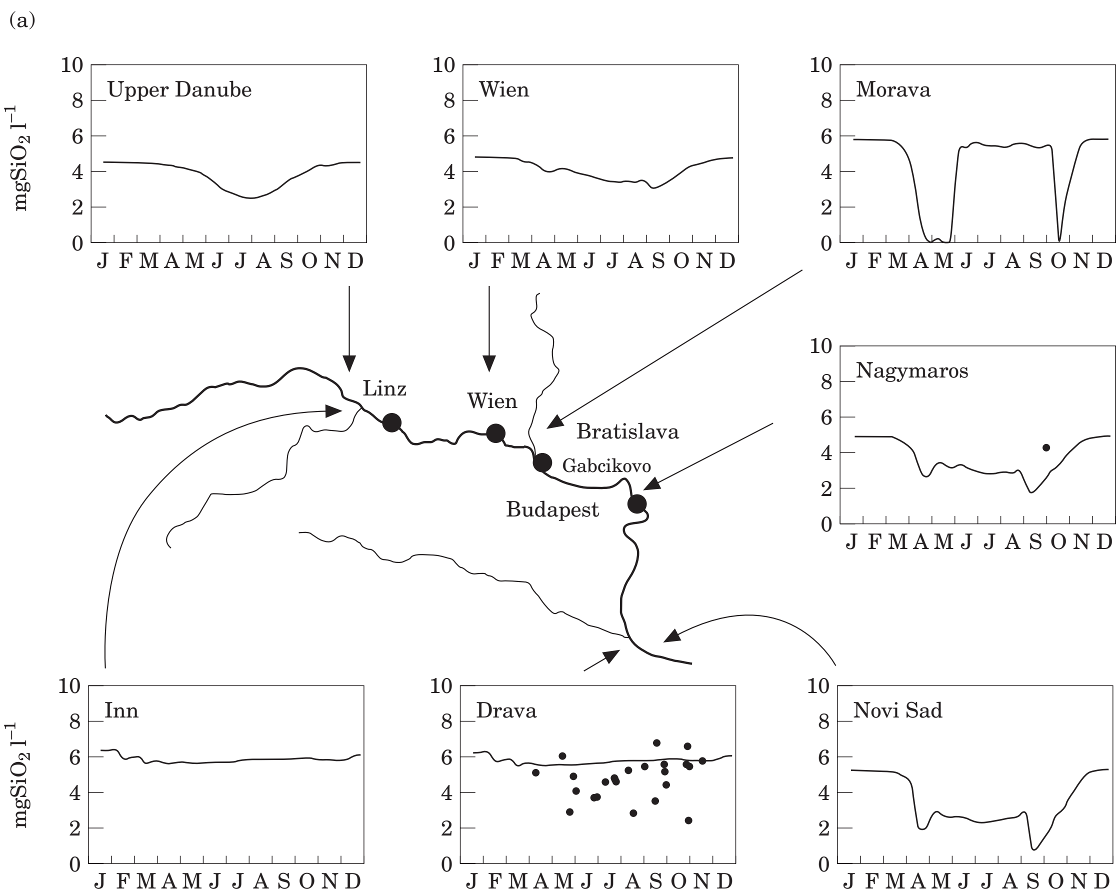

FIGURE 11. (a). *Continued on p. 305.*

TABLE 8. Calculated budget of nutrient input, transfer and delivery by the Danube River system for a scenario of P and N reduction, characterizing the post-reference period of decline in economic activity

	kgTN yr^{-1}		kgTP yr^{-1}			
	Total N	NO_3+NH_4	Total P	PO_4	kgTSi yr^{-1}	Si/Total P (w/w)
Non-point sources						
Model calculations	456		29		502	17·3
Point sources						
Model calculations	516		87		0	—
Output to the Black Sea						
Model calculations	710	644	35	15	352	10
Observed 1994–1996[a]		530		12	218	—

[a]Observed delivery during 1994–1996 (Cociasu *et al.*, 1996 and pers. comm.).

have reduced the recorded nutrient release associated with industrial activity by these proportions in the corresponding sub-basins.

Another change is the significant reduction in the use of P-containing detergents, either as a result of overall economic recession (in most countries of the former Eastern Bloc) or of a deliberate policy of replacement by other products (as in Austria).

Finally, a decrease in the use of fertilizers, concomitant with economic changes (Masaryk & Varley,

(b)

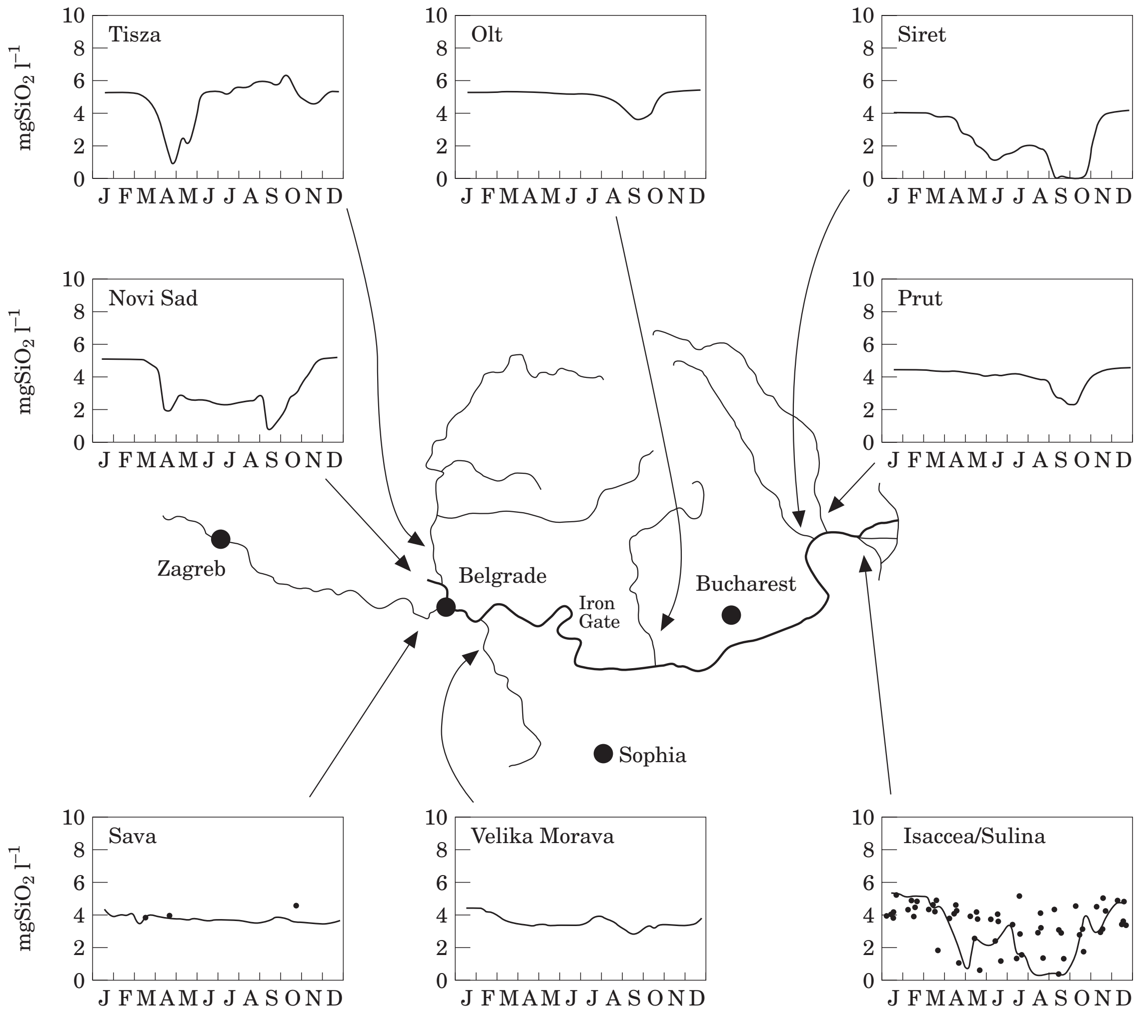

FIGURE 11. (b).

FIGURE 11. (a) Upper and (b) lower course of the Danube River. Simulation by the RIVERSTRAHLER model of seasonal silica variations for the period 1988–1990. Experimental data for the same period are given for comparison.

1997), is taken into account in our scenario, with a 20% reduction of diffuse nitrogen sources in Hungary and Slovakia, and a 40% reduction in Romania. The resulting nutrient budget (Table 8) agrees remarkably with the data reported for the years 1994–1996 (Cociasu *et al*., 1996).

Conclusion

Within its limits of validation, the RIVERSTRAHLER model has correctly simulated the seasonal levels and fluxes of the major water-quality variables for the period 1989–1991. Based on realistic hypotheses, the model also correctly reproduces the reduction in P and N delivery related to recent economic changes in the region. However, these changes have not been validated at the scale of the 10 sub-basins, which considerably differ in their geographical characteristics and recent socio-economical trends. Neither did we include in the model the effect of the Gabcikovo reservoir, which could have modified the water quality since it started operating in 1994. Nevertheless, the model as it stands, once it has been correctly validated on more extensive water-quality databases, constitutes a useful tool for further exploring the effects, at the basin scale, of the rapid changes of human activity occurring in this region of the world.

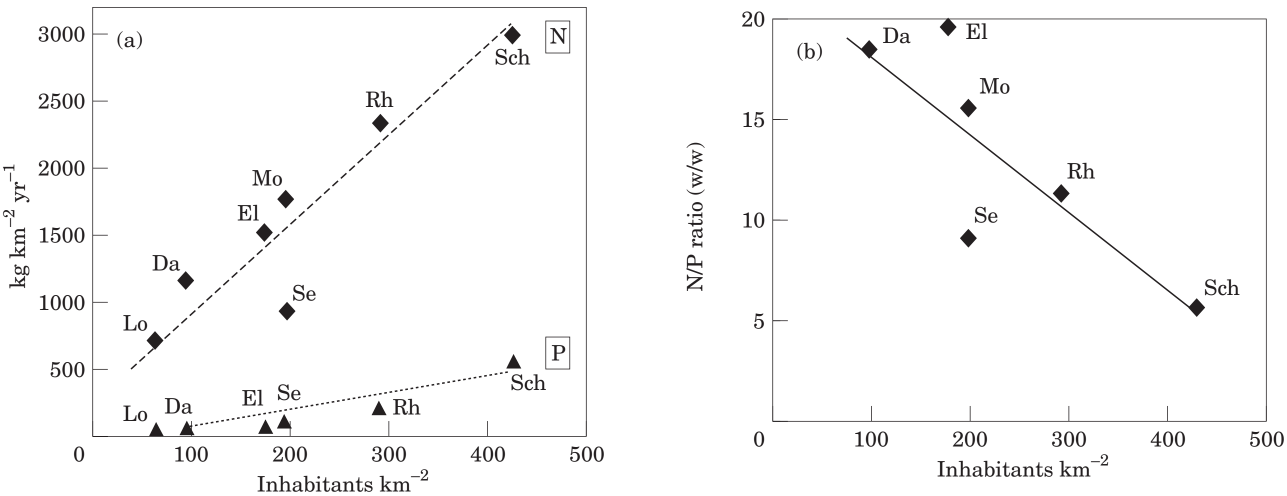

FIGURE 12. (a) Relationship between specific fluxes of nitrogen and phosphorus (kgN or P km^{-2}) and population density (inhabitants km^{-2}). (b) Relationship between N/P ratio and population density. Da: Danube River; El: Elbe River; Lo: Loire River; Mo: Mosel River; Rh: Rhine River; Sch: Scheldt River; Se: Seine River.

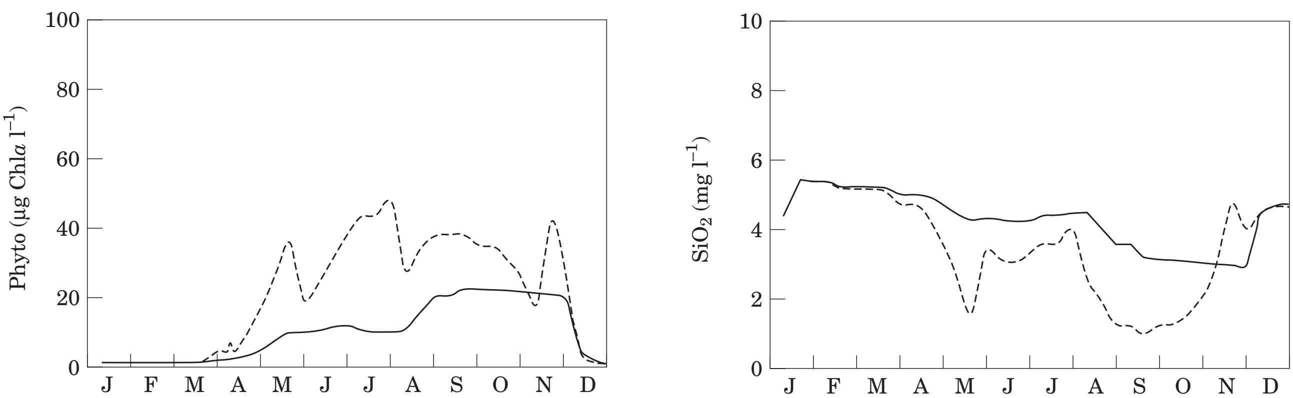

FIGURE 13. Simulations by the RIVERSTRAHLER model of phytoplankton biomass (Chl *a*) and silica concentrations (SiO_2) at the outlet of the Danube River in a scenario with 90% abatement of total phosphorus point sources. Results for the reference situation are given for comparison. (----) Reference 1988–1991; (——) 90% Ptot reduction.

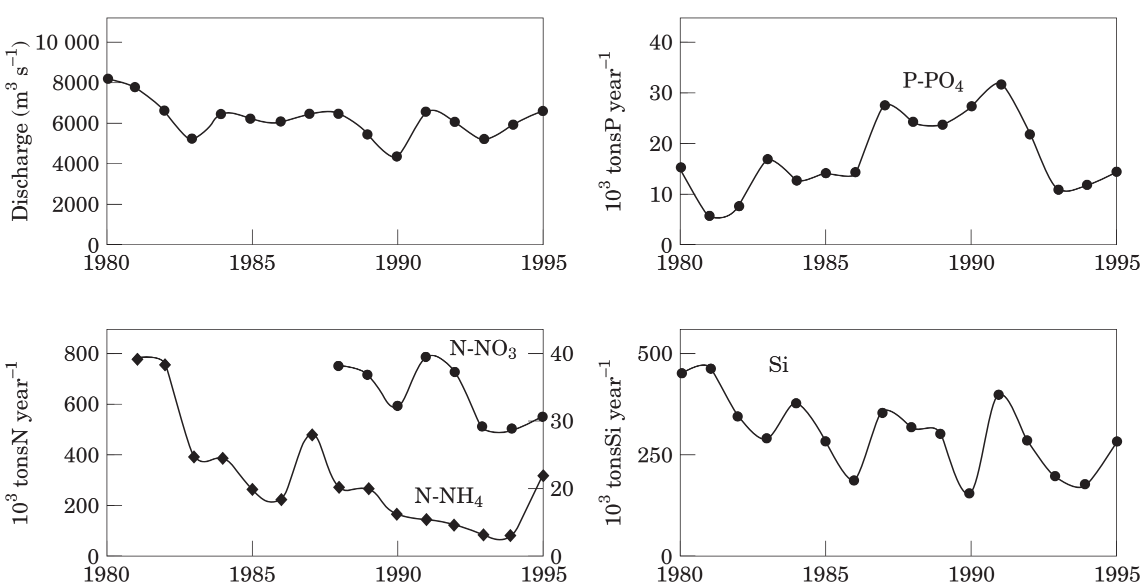

FIGURE 14. Interannual variations in water discharges and nitrogen (N-NO_3 and N-NH_4), phosphate (P-PO_4) and silica (Si) fluxes at the outlet of the Danube Basin (data from Cociasu *et al.*, 1996).

Acknowledgements

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