HYDROLOGICAL PROCESSES
Hydrol. Process. **15**, 587–593 (2001)
DOI: 10.1002/hyp.168

Particulate heavy metal transport in the lower Paraíba do Sul River basin, southeastern, Brazil

M. S. M. B. Salomão,[1] M. M. Molisani,[1] A. R. C. Ovalle,[1] C. E. Rezende,[1] L. D. Lacerda[2] and C. E. V. Carvalho[1]*

[1] *Laboratório de Ciências Ambientais - CBB, Universidade Estadual do Norte Fluminense, Av. Alberto Lamego 2000, Horto, Campos dos Goytacazes, R.J. CEP 28015-620, Brasil*
[2] *Departamento de Geoquímica, Universidade Federal Fluminense, Niteroí, R.J., Brazil*

Abstract:

In the present study an attempt has been made to calculate the mass transfers of suspended particulate matter and associated heavy metal within the lower portion of the Paraíba do Sul River drainage basin and the contribution of its tributaries. The highest metal loads were related with the highest water flows and, consequently, with the highest suspended particulate matter loads, which increased both by surface runoff and sediment resuspension. The highest flow month for the total transported load contributed between 34 and 66% of the total metal transported per year. The total load transported during the entire rainy season ranges from 82 to 93% of the total transported load. The importance of the tributary input for the total transported load of the Paraíba do Sul River was generally lower than 10%, although in some months, when the Paraíba do Sul River had low water discharge and strong local rain occurred, this increased upto 40%. Copyright © 2001 John Wiley & Sons, Ltd.

KEY WORDS suspended particulate matter; heavy metals; tropical river; fluxes; mass balance

INTRODUCTION

Heavy metal contamination in aquatic environments has already been widely studied and described by several authors (Salomons and Forstner, 1984; Foster and Charlesworth, 1996). In fluvial systems, suspended particulate matter plays an important role in the transport and accumulation of metals, mainly as a result of their high surface area and the presence of oxide coatings (Jenne, 1968; Warren and Zimmerman, 1993).

Small and medium sized rivers, though quite significant in terms of mass transfer, generally have not been considered in attempts to quantify global mass transfers (Holeman, 1968; Meybeck, 1976; Martin and Meybeck, 1979; Milliman and Meade, 1983). The reliability of the global budget is further compromised by the lack of a proper data base from third world rivers. A detailed monitoring of rivers on local and regional scales will surely improve the knowledge in terms of global mass transfer (Jah *et al.*, 1988).

In the present study an attempt has been made to calculate the mass transfers within the lower portion of the Paraíba do Sul River drainage basin and the contribution of its tributaries.

STUDY AREA

The Paraíba do Sul River (PSR) is a medium size river, with a length of approximately 1145 km and a watershed area of 55 400 km^2. The river drains the most industrialized states of Brazil: Rio de Janeiro, São Paulo and Minas Gerais. The climate is subtropical with a rainy season in the summer.

* Correspondence to: Dr C. E. V. Carvalho, Laboratório de Ciências Ambientais - CBB, Universidade Estadual do Norte Fluminense, Av. Alberto Lamego 2000, Horto, Campos dos Goytacazes, R.J. CEP 28015-620, Brazil. E-mail: carvalho@cbb.uenf.br

Received 21 February 2000
Accepted 28 June 2000

The pluviometric regime is well characterized and the period between November and January is when the rainfall is highest, and when large floods of the Paraíba do Sul River occur. The period between June and August is the driest of the year. Maximum river flow is observed during summer (4380 m^3/s) and the lower discharges generally occur in the winter (180 m^3/s) (DNAEE,1983; Rosso *et al.*, 1991). The PSR water is very important to the cities located in its watershed, where it is widely used in agriculture, industry and for human consumption (over 20 million people live in the watershed). On the other hand, the river receives effluents from all these activities, generally without efficient treatment.

The main tributaries of the lower PSR are: Pomba, Dois Rios and the Muriaé Rivers (Figure 1). This portion of the PSR basin is dominated geologically by gneiss in the Itaocara region and by an undulating relief. Downstream of São Fidélis City the relief becomes plain and is composed of Quaternary fluvial deposits. Land use is basically urban development, agriculture, extensive cattle farming and small fragments of natural vegetation (Projeto RADAMBRASIL, 1983).

Previous research in the middle reaches of the Paraíba do Sul River showed critical concentrations of some elements (Pb, Cu, Cr and Zn) in suspended particulate matter (Malm, 1986), although more recent research has shown that the lower Paraíba do Sul River drainage basin has low or no metal contamination in the

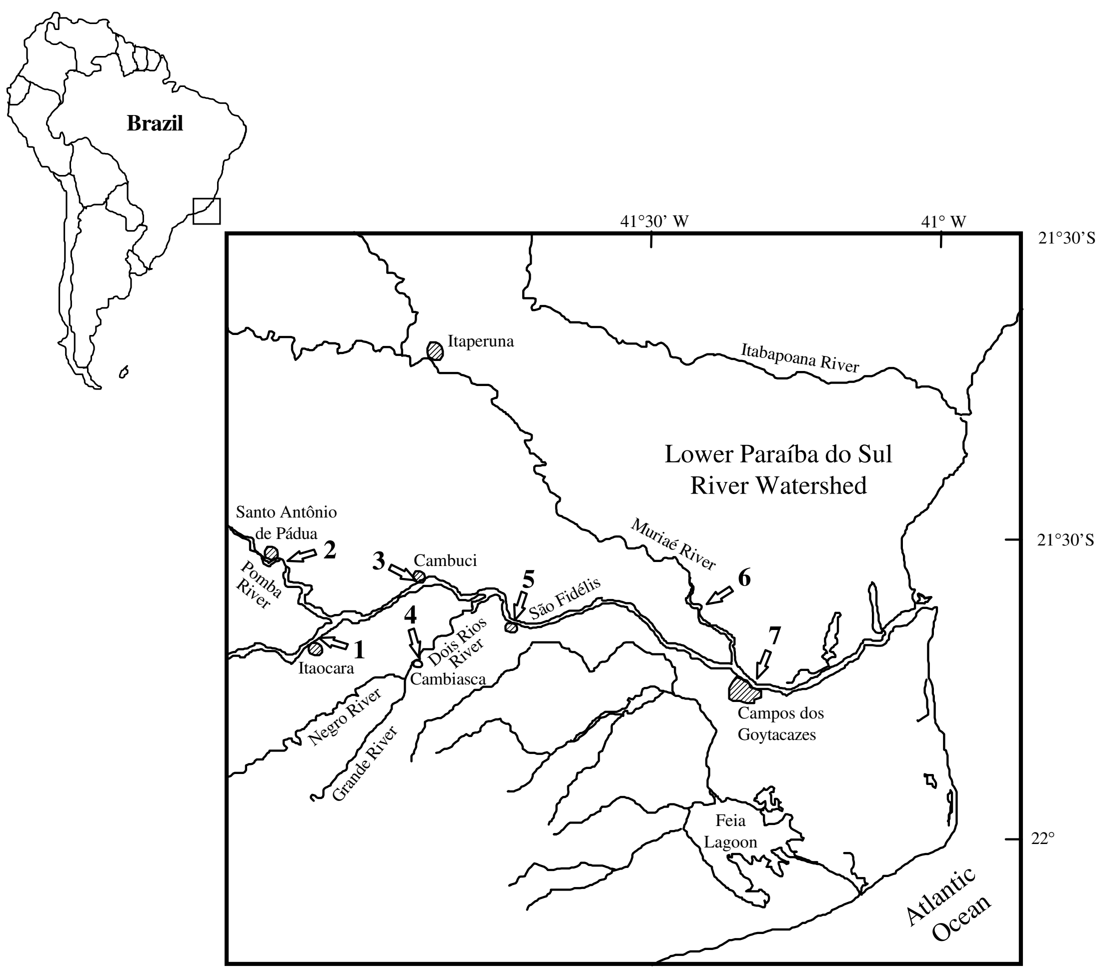

Figure 1. Sampling site locations. Hatched areas represents the main cities in the area

suspended sediments (Carvalho *et al.*, 1999; Molisani *et al.*, 1999). The main process that seems to regulate the seasonal variation is the dilution effects caused by the change in the source of the suspended particulate matter (runoff input versus industrial input).

MATERIALS AND METHODS

Sampling

Seven stations were selected along the PSR drainage basin (Figure 1), four in the PSR itself (stations 1, 3, 5 and 7), and the other three (stations 2, 4 and 6) in the main tributaries of the PSR lower basin, Pomba, Dois Rios and Muriaé Rivers (Figure 1). The sampling generally took 3 days, mainly as a result of the large distances between the sampling stations, roads in bad conditions and the small sampling group (two researchers). Detailed information on sampling strategies and background information on catchment hydrology can be found in Carvalho *et al.* (1999) and DNAEE (1983).

Samples were collected monthly over 24 months. In the first 12 months (from April 1994 to March 1995) all seven points were sampled, and in the following 12 months (July 1995 to March 1996) only station 7 was sampled.

All the water samples were collected with a polyethylene 'Van Dorn' type sampler and stored in 10-l polyethylene flasks, which were kept on ice during transport to the laboratory. The samples were filtered in triplicate (Millipore cellulose acetate 0·45 μm of pore diameter), and oven dried (80 °C/48 h) for subsequent acid digestion and metal analysis.

The filters were digested following a modified version of the procedure used by Watts and Smith (1994). The filters were placed in Teflon bombs, with hot concentrated acids ($HCl + HNO_3 + HF$). After total dissolution of the sample, the acid was evaporated to almost dryness, and redissolved with HCl 0·5M (25 ml). The extracts were than analysed by conventional flame atomic absorption spectrophotometry.

The coefficient of variation (CV) for triplicates of the same sample was generally lower than 20%. If the CV was higher than 20%, another replicate was analysed in order to check the values. Two standard reference materials were analysed in order to estimate the accuracy of the digestion method (riverine sediment Standard Material 2704 and estuarine sediment Standard Material 1646a), both supplied by the National Institute of Standards and Technology (USA). Heavy metal recovery rates are shown in Table I.

River flow measurements were performed monthly with one or more coupled flow meters (General Oceanic model 2030). Riverine cross-section areas were calculated, based on the bathymetric measurements. After mapping the cross-section of the river, each section was divided into two to four subsections, where the current meters were installed. In each subsection the current meters were positioned at different depths starting from 1·5 m from the bottom to the surface in order to minimize the error caused by the differences in velocity from the river bed to surface (Kjerfve *et al.*, 1981).

A mass balance estimation was performed in order to determine the volume of water and the mass of suspended particulate matter and heavy metals moved by the Paraíba do Sul River and its tributaries, following

Table I. Recovery percentage of the total metals in two standard materials

Standard material	Cu	Cr	Zn	Mn	Fe
River sediment[a] (Standard Material 2704)	103	90	91	87	86
Estuarine sediment[a] (Standard Material 1646a)	95	85	105	91	90

[a] Standard material supplied by the National Institute of Standards and Technology (USA).

the method described by Kjerfve *et al.* (1981). The measured water discharge values were assumed to be constant between two sampling periods and the total estimated flux for each year was obtained from the sum of the values obtained for each month (Woodroffe, 1985).

Figueiredo (1999), working in the same area and at the same sampling sites, compared the monthly measured fluxes of diverse chemical species (COP, NOP, DIC, DOC, N-NO_3, N-NO_2, N-NH_4 and DON) and suspended particulate matter (SPM) at the gauging station 7 (Campos) calculated by two method. The first assuming that the chemical species concentration remains constant between two sampling periods (30 days) but using daily water discharge data calculated with rating curves from DNAEE. The second method assumed that both concentration and water discharge were constant between the two samplings. The results obtained showed a very low variation between both method. The first method always presented higher fluxes than the second, the minimum flux difference was 5% (DIC) and the maximum difference was 15% (POC, PON and SPM). Although the maximum difference between the two method was up to 15%, no statistically significant difference was apparent between daily discharges measured by rating curves from DNAEE and the method used in this study ($P < 0{\cdot}001$, Wilcoxon Test, $n = 26$).

RESULTS AND DISCUSSION

The annual heavy metals loads for all the four stations along the Paraíba do Sul River and its tributaries (Pomba, Dois Rios and Muriaé Rivers) are presented in Table II. The sampling period was the same for all the sites, from April 1994 to March 1995, except for station 7 (Campos), when a longer period was observed, from April 1994 to March 1996.

The monthly metal loads were highly variable (e.g. station 7, Table III). In general, the highest loads were related to months with the highest water discharges and, consequently, with the highest suspended particulate matter loads. This observation reinforces the importance of suspended particulate matter as the main carrier for heavy metals in rivers, as described my many authors (Jenne, 1968; Warren and Zimmerman, 1993). It is also important to note the importance of the highest flow month for the total transported load. In the case of station 7 (Campos) February contributed from 34 to 66% of the total mass transported. If we calculate the total load transported separately during the rainy season and the dry season, however, the data show that between 82 and 93% of the total load is transported during the rainy season.

The general behaviour of the monthly metal loads was similar between the stations of Paraíba do Sul River and the tributary rivers, although with some small differences. In all the stations of the Paraíba do Sul River, as well as those of its tributaries, the highest loads were always observed during higher water flow (stations 1

Table II. Suspended particulate matter (SPM) and metal loads of the Paraíba do Sul River and its tributary stations over the sampling period (from April 1994/March 1995)

Sampling station	Cu (ton)	Cr (ton)	Zn (ton)	Mn (ton)	Fe (ton)	SPM (ton)
1 PSR Itaocara	67	25	113	826	46 558	648 037
3 PSR Cambuci	101	48	174	1284	85 139	895 679
5 PSR S.Fidélis	42	33	165	952	65 506	890 234
7 PSR Campos	87	47	197	1350	68 228	821 489
7 PSR Campos[a]	137	162	483	3241	145 323	2 042 080
2 Pomba River	14	10	23	249	13 490	163 036
4 Dois Rios River	13	4	13	182	8378	103 925
6 Muriaé River	3	4	10	136	5886	69 232

[a] Second sampling period (from April 1995 to March 1996).

Table III. Monthly heavy metals and suspended particulate matter loads transported by Paraíba do Sul River at station 7 (Campos)

Station 7 Campos	Cu (%)	Cr (%)	Zn (%)	Mn (%)	Fe (%)	SPM (%)
April[a]	5·5	21·5	26·9	18·7	14·1	13·8
May[b]	1·6	3·8	4·8	5·3	4·7	4·2
June[b]	2·1	4·0	3·4	5·4	4·5	4·3
July[b]	1·5	2·8	1·4	2·7	1·9	2·1
August[b]	0·9	1·5	1·2	1·2	0·4	1·0
September[b]	0·3	0·6	1·1	2·0	0·6	0·9
October[b]	0·6	1·1	0·8	1·0	0·5	0·8
November[a]	5·3	3·8	4·0	4·9	3·9	4·5
December[a]	7·7	8·9	12·3	5·7	5·3	6·5
January[a]	6·7	4·9	7·8	6·1	5·6	5·3
February[a]	66·0	42·8	34·0	42·8	55·5	52·2
March[a]	1·7	4·0	2·3	4·1	3·0	4·4
Rainy period[a]	92·9	85·9	87·3	82·3	87·4	86·7
Dry period[b]	7·1	14·1	12·7	17·7	12·6	13·3

(Itaocara), 3 (Cambuci), 5 (São Fidélis), and 7 (Campos), in February 1995 and in January 1996 for station 7 (during the second observation period)). The Dois Rios River showed the same behaviour as that described for the Paraíba do Sul River stations, achieving higher flows in the month of February 1995, although in December 1994, the Dois Rios River had high flows in spite of the low contribution from Paraíba do Sul River. This month had the largest influence of this river in relation to Paraíba do Sul River. In the other two tributaries a different behaviour was observed. The Pomba and Muriaé Rivers had their higher water flows in April 1994.

The lowest water flows and loads in most of the cases occurred between May and July 1995 for all the stations of the Paraíba do Sul River, as in its tributaries.

The importance of the tributary inputs for the total transported load of the Paraíba do Sul River generally did not exceed 10%, although in some months, where the Paraíba do Sul River had low water flux and strong local rain occurred, this contribution increases up to 40% of the total transported load of RPS (e.g. December 1994, Dois Rios River, Figure 2).

The total flux of heavy metals transported by the Paraíba do Sul River drainage basin was calculated at station 7 (Campos). Comparing the two periods it is observed that in the second period (from April 1995 to March 1996) loads were more than 100% greater than the first period (from April 1994 to March 1995). This fact was observed not only for the suspended particulate matter but also for all the metals studied. The explanation is probably linked to the annual rainfall. The first period (from April 1994 to March 1995) was characterized by very little rainfall (733 mm) and could be considered as a dry year. The second period (from April 1995 to March 1996) had higher rainfall (779 mm) but it was also lower than the average rainfall for the region (890 mm/year). This observation is confirmed in Figure 3 where the maximum, average and minimum discharge curves calculated by DNAEE, based on information obtained in measurements during the period of 1934 to 1978, were compared with the values measured during this study. Based on these two observations it is possible to conclude that the sampling period of this study is representative of years of low rainfall and river discharge.

The monthly load variations showed a strong dependence on rainfall and, consequently, with surface runoff. However, in some months it was observed that the increase in the load among two consecutive Paraíba do Sul river sampling stations (e.g. stations 3 and 5) could not be explained just by the contribution of a tributary located between them (e.g. Dois Rios). This observation probably reflects the importance of bottom sediment

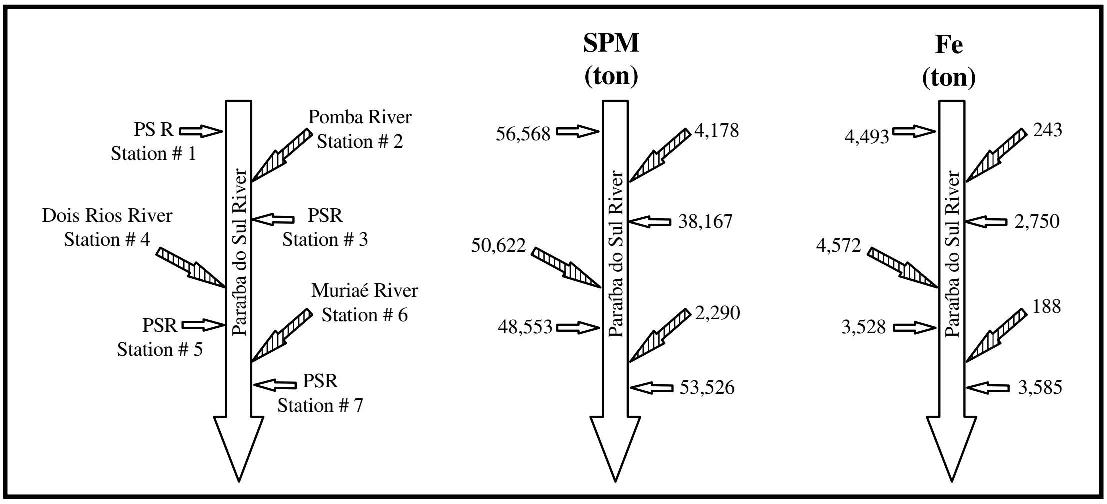

Figure 2. Schematic representation of the suspended particulate matter (SPM) and Fe loads transported along the mainstream (solid arrows) and tributaries (hatched arrows) in December 1994

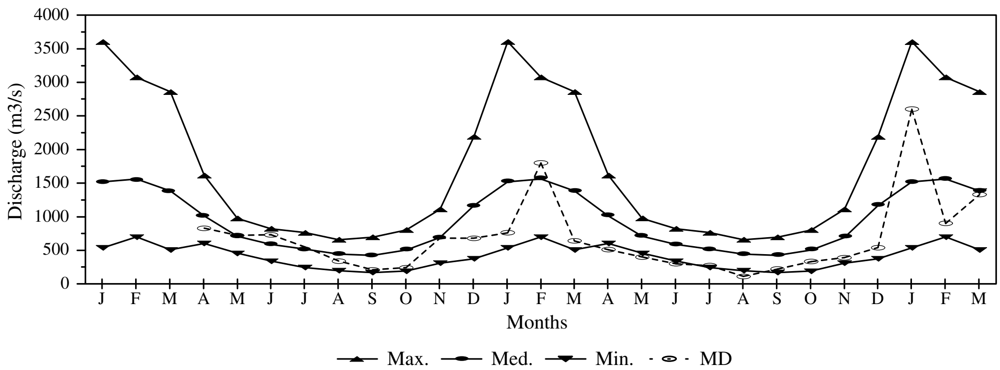

Figure 3. Maximum, average and minimum discharges curves calculated by DNAEE for station 7 (1934 to 1978) compared with the measured discharges during this study (MD)

resuspension, although more studies are needed in order to precisely define the importance of resuspension in the system.

CONCLUSIONS

In general, the highest loads were related to the highest water flows and, consequently, with the highest suspended particulate matter loads. The importance of the tributary inputs for the total transported load of the Paraíba do Sul River generally was generally lower than 10%, although in some situations it could reach up to 40%.

ACKNOWLEDGEMENTS

The authors would like to thank FENORTE and FAPERJ (CEVC, proc. no. 170.701/95) for the financial support.

REFERENCES

Carvalho CEV, Ovalle ARC, Rezende CE, Salomão MSMB, Molisani MM, Lacerda LD. 1999. Seasonal variation of particulate heavy metals in the Lower Paraíba do Sul River Drainage Basin, R.J. Brazil. *Environmental Geology* **37**(4): 297–302.

DNAEE. 1983. *Boletim Fluviométrico F-5.02, Bacia do Paraíba do Sul*. Departamento Nacional de Águas e Energia Elétrica. 786.

Figueiredo RO. 1999. *Transporte de Carbono e Nitrogênio no Baixo Paraíba do Sul: Fluxos e Processos*. PhD thesis, Universidade Estadual do Norte Fluminense, Campos, Brazil; 177 pp.

Foster IDL, Charlesworth SM. 1996. Heavy metals in the hydrological cycle: trends and explanations. *Hydrological Processes* **10**: 227–261.

Holeman JN. 1968. Sediment yield of major rivers of the world. *Water Resources Research* **4**: 737–747.

Jah PK, Subramanian V, Sitasawad R. 1988. Chemical and sediment mass transfer in the Yamuna River—a tributary of the Ganges System. *Journal of Hydrology* **104**: 237–246.

Jenne EA. 1968. Controls on Mn, Fe, Co, Ni, Cu and Zn concentrations in soil and water: the significant role of hydrous Mn- and Fe-oxides. *American Chemical Society Advances in Chemistry Series* **73**: 337–387.

Kjerfve B, Stevenson JA, Phoehl TH, Chrznowski TH, Kitchens WH. 1981. Estimation of material fluxes in an estuarine cross-section: a critical analysis of spatial measurements density and errors. *Limnology and Oceanography* **26**: 325–333.

Malm O. 1986. *Estudo da poluição ambiental por metais pesados no sistema Rio Paraíba do Sul-Rio Guandú (RPS-RG) através da metodologia de abordagem pelos parâmetros críticos*. MSc thesis, IBCCF, UFRJ; 127 pp.

Martin JM, Meybeck M. 1979. Elemental mass-balance of material carried by major world rivers. *Marine Chemistry* **7**: 173–206.

Meybeck M. 1976. Total mineral dissolved transport by major world rivers. *Hydrological Sciences Bulletin* **21**(2): 265–284.

Milliman JD, Meade RH. 1983. World-wide delivery of river sediment to the oceans. *Journal of Geology* **91**(1): 1–21.

Molisani MM, Carvalho CEV, Ovalle ARC, Rezende CE, Salomão MSMB, Lacerda LD. 1999. Heavy metals distribution in sediments of the lower Paraíba do Sul River and Estuary—RJ., Brazil. *Bulletin of Environmental Contamination and Toxicology* **63**(5): 682–690.

Projeto RADAMBRASIL. 1983. Folhas SF.23/24 Rio de Janeiro/Vitória; geologia, geomorfologia, pedologia, vegetação e uso potencial da terra. Rio de Janeiro; 780 pp. and 6 maps.

Rosso TCA, Neves CF, Rosman PCC. 1991. O estuário do Rio Paraíba do Sul: Perspectivas em um cenário de variação do nível do mar. *Simpósio Brasileiro de Recursos Hídricos 9 and Simpósio LusoBrasileiro de Hidráulica e Recursos Hídricos 5*, Rio de Janeiro, Editora da ABRH, **3**: 578–586.

Salomons W, Föstner U. 1984. *Metals in the Hydrocycle*. SpringerVerlag: Berlin; 349 pp.

Warren LA, Zimmerman AP. 1993. Trace metal/SPM associations in a fluvial system: physical and chemical influences. In *Particulate Matter and Aquatic Contaminants*, Rao SS (ed.). Lewis Publishers; 425 pp.

Watts SEJ, Smith BJ. 1994. The contribution of highway runoff to river sediment and implications for the impounding of urban estuaries, a case study of Belfast. *The Science of Total Environment* **146/147**: 507–514.

Woodroffe CD. 1985. Studies of mangrove basin, Tuff Crater, New Zealand: II. Comparison of volumetric and velocity-area methods of estimating tidal flux. *Estuarine and Coastal Shelf Science*, **20**: 431–445.

