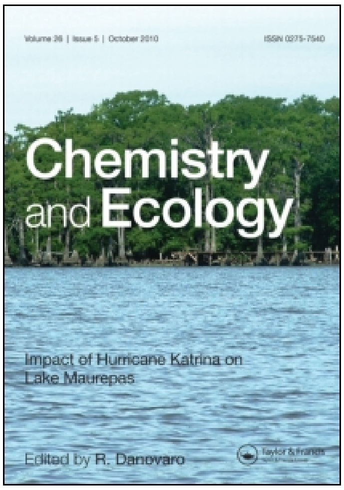

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THE ROLE OF SUSPENDED MATTER IN ASSESSING THE ASSIMILATIVE CAPACITY

Case Study of Two Estuaries in the Adriatic Sea

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Suspended particulate matter has been studied in two Adriatic river mouths to assess its role as a transport vehicle for waste disposal into the Adriatic sea.

The larger of the two, the Adige River (northwestern Adriatic coast, Italy), carries large quantities of solids and builds up a prodelta. The Krka River (eastern Adriatic coast, Croatia, Yugoslavia) is a typical karst river, and carries small quantities of suspended matter, since it drains carbonate terrains.

The resulting disposal of contaminants into the Adriatic sea is largely governed by the adsorption/desorption processes occurring in the estuarine mixing region. Surface adsorption properties, the specific surface area, and the nature and reactivity of the organic film coating determine the partitioning of pollutants between the dissolved and particulate state.

In the Adige River mouth, lead, chromium, zinc, and nickel are accumulated in the prodelta sediments, and thus the loading of the sea with these metals is diminished, whereas in the Krka River estuary, desorption and mobilization of some trace metals occurs.

The observations reported point to the key role of particulates in transport of pollutants from land to sea. The concept of the assimilative capacity of the estuarine area requires detailed scientific knowledge on the geochemical behaviour of particulates.

INTRODUCTION

There is controversy in the literature on the concept and the possibility of assessment of the assimilative (*environmental, absorptive, receiving*) capacity of any specific segment of the aquatic (marine, estuarine or other) environment. The controversy is both a matter of principle and relates to the possible use of this "capacity" for waste management (Goldberg, 1979; GESAMP, 1986; Pravdić and Juračić, 1988; IUCN, 1990; Krom *et al.* 1990b).

As a matter of principle, the assimilative capacity approach requires a quantitative knowledge of all significant and relevant processes of geochemical cycling of a pollutant, and of course of all the pollutants discharged to the impacted area.

As a matter of use for waste management the concept has been criticized as an "invitation to pollute", and considered as superfluous and ineffective, and unsuitable as a strategy to combat marine pollution in view of such regulatory

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concepts as uniform emission standards (*UES*) (Marinov and Jernelov, 1987; Greenpeace International, 1990).

This paper advocates the use and the application of assimilative capacity through a gradual scientific approach to the understanding of the various selective processes that dominate the geochemical fate of major pollutants. In the context we describe here the role of suspended matter in transference and partitioning between the solid and the liquid phase, and the overall behaviour of contaminants and pollutants in two different river mouths in a semi-enclosed sea, the Adriatic. There is ample evidence in the literature (Stumm and Morgan, 1981; Foerstner, 1983; Salomons and Foerstner, 1984; Krom *et al.* 1990a; 1990b; Nyffeler, 1990; Nolan and Fowler, 1990; Pravdić *et al.*, 1990) on the crucial role of land-based particulate matter in influencing the geochemical behaviour of pollutants in coastal areas.

The aim of this paper is also a generalization from observations made at two specific locations and the recognition of suspended matter as a major component of the total assimilative, or environmental capacity.

METHODOLOGY OF THE APPROACH

In this paper we present selected results obtained in the Krka river estuary and the Adige river mouth (Juračić, 1987; Pravdić and Juračić, 1988; Boldrin *et al.* 1989; Prohić and Juračić, 1989) with the aim of clarifying the role of suspended matter in the assessment of the assimilative capacity.

Sampling, sample treatment and analytical measurements were based on standard techniques described elsewhere (Juračić, 1987; Boldrin *et al.* 1989; Biščan *et al.* 1991). Briefly, suspended matter samples were collected by filtration of large samples of river water (up to 1000 litres; Stations 1 in Figures 1B and 1C); sediments in the accumulation zone (Stations 4 and 5, Figure 1B; and Stations 2 and 3 in Figure 1C) were collected by scuba diving or by using box corers, taking advantage of the shallowness of the area. In the laboratory the physicochemical characterization was made by granulometry, organic matter content, determination of the specific surface area, and analysis of selected heavy metals.

REVIEW OF RESULTS

The area of investigation is identified in Figure 1; Figure 1A locates the investigated areas in the Adriatic; Figure 1B identifies the sampling locations in the Adige River mouth; Figure 1C identifies those in the Krka River estuary.

In Table 1 the comparison of the main characteristics of the Adige and Krka rivers are presented. The Adige is the second largest river draining into the Adriatic. The drainage area of the Adige River is composed mainly of clastic sedimentary, eruptive and metamorphic rocks. Therefore, the river carries a large suspended matter and bed load, due to soil erosion and the geological composition of the area. The river drains a heavily industrialized and intensively cultivated area with a population of approx. 1.6 M inhabitants. The Adige River

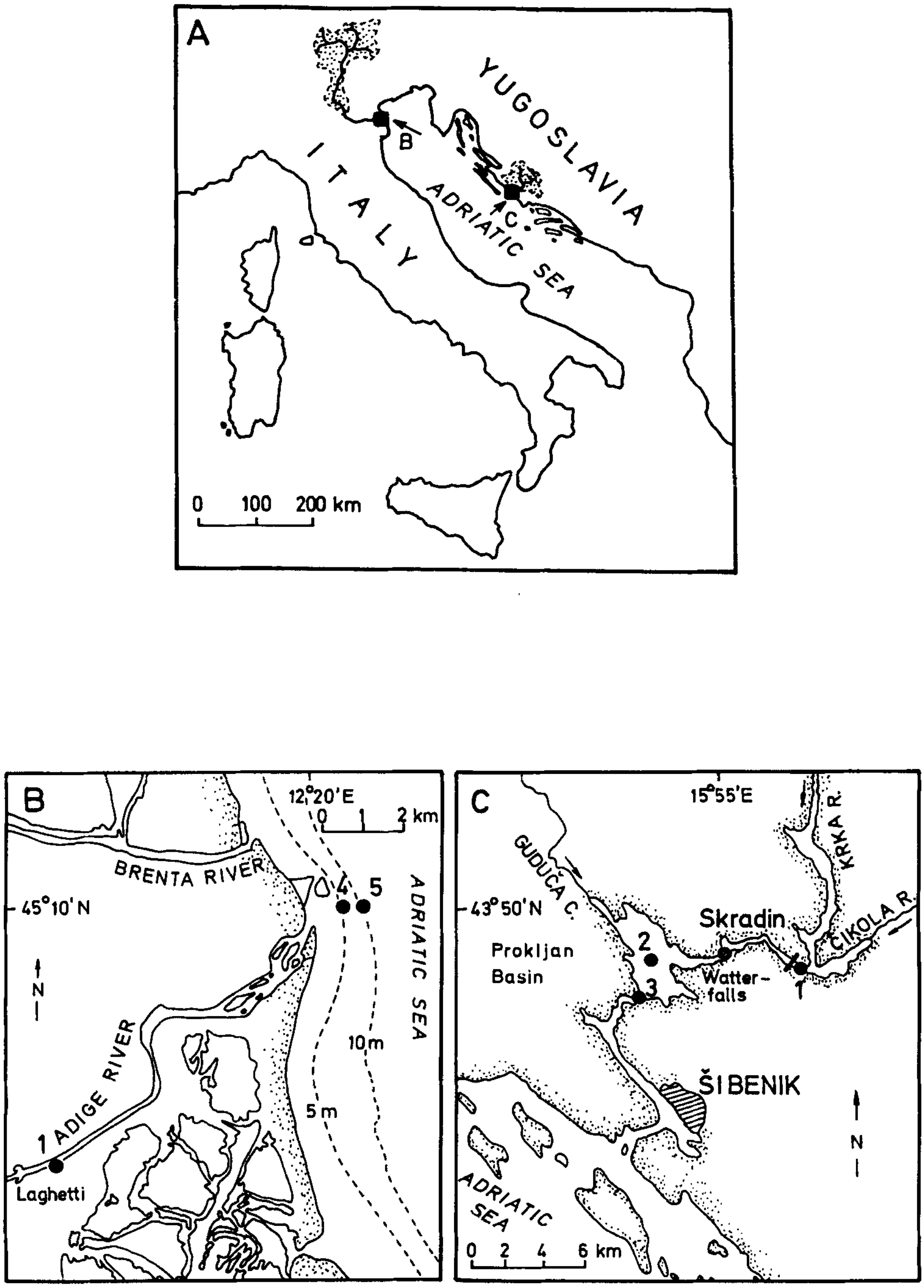

Figure 1 A: Identification of the rivers and their drainage areas. B: Sampling stations at the Adige River mouth. C: Sampling locations in the Krka River estuary.

Table 1 Comparison of main characteristics of the Adige and Krka Rivers†

	Adige River	*Krka River*
River length, km	400	72
Drainage area, km^2	12,000	2427[1]
Mean water flow, $m^3 s^{-1}$	207	49
(range)	80–900	4–415
Transport of solids, $t\,y^{-1}$	886×10^3	5×10^3
Concn. of solids, $mg\,l^{-1}$	136	2.5
(range)	10–300	1–4
Mouth type	neutral/delta	estuary

† Data compiled from: Juračić *et al.* (1987); Juračić (1987); Prohić and Juračić (1989); Cauwet (1991).

[1] Hydrogeologic drainage area (Stepinac, 1976); topographic drainage area = 2088 km^2 (Šimek-Škoda, 1978).

mouth is characteristic for the northern and northwestern part of the Adriatic coast: it is not a typical delta mouth, although it has some deltaic accretion (Figure 1B). Its range of water flow varies through an order of magnitude due to hydrogeologic and climatic conditions.

The Krka River estuary, in the eastern-middle Adriatic, is a typical highly stratified estuary, with a very low input of particulate matter. It is typical for the whole eastern Adriatic coast, where carbonate rocks (karst) predominate. The water flow varies by two orders of magnitude, another characteristic of karst rivers. The drainage area is difficult to define, due to the specific water movement in the karstic carbonate rocks. This is due to the fact that topography is not always the hydrogeological barrier. Corrosion and dissolution are the main weathering processes, rather than rock decomposition, and therefore a very low concentration of solids is found in karst rivers. Moreover the calc-tufa (travertine) barriers, which build up in the Krka River canyon, limit the amount of particulate matter transported to the estuary. The river receives effluents of a small city with metal manufacturing industries, and the outflow from an area, small in size but of intensive agricultural activity.

Thus, the Adige River mouth is of the neutral/delta type (nomenclature according to Seibold and Berger, 1982), whereas the mouth of the Krka River is a typical karst estuary.

Table 2 shows a comparison of data for the riverine suspended matter and prodelta sediments (zone of accumulation of riverine material) for the two rivers. Grain sizes of sediments in the Adige River prodelta are roughly twice the size of those in the Krka river estuary. The mineral composition reflects the differences of the source area. Suspended matter in the Adige River is principally quartz and aluminosilicates, whereas in the Krka River, calcite grains prevail. The limited availability of suspended matter of terrestrial, mineral origin, leads to a large fraction of particles of organic origin in the Krka River suspended matter.

The specific surface areas reflect both the mineral composition and the grain size distribution. The specific surface area of the suspended matter for the Adige River samples is larger than the corresponding value for the sediments. The opposite is true for the Krka River, where the prodelta sediments have very large specific surface areas, in excess of $30\,m^2\,g^{-1}$.

Inspection of the geochemical data for selected heavy metals in Table 2

Table 2 Characteristics of suspended matter and sediments†

	Adige River		*Krka River*	
	Suspended[1]	*Sediments*[2]	*Suspended*[3]	*Sediments*[4]
Mean grain size, μm	7–8	8–16	n.a.	5–7
Main mineral species	quartz, alumino–silicates	alumino–silicates, quartz	calcite,	calcite alumino–silicates
Organic matter, %	3–5	6–7.5	15–30	4.5–5.5
Specific surface area, $m^2 g^{-1}$:				
native	3–12	4–6	8–19	30–35
treated	10–20	9–11	n.a.	28–32
Trace metal concn. μg/g				
Cu	47–50	47–60	180	42–45
Pb	49–78	38–42	92	30–48
Cr	126–159	125–221	150	37–60
Zn	213–270	173–221	210	34–50
Ni	32–42	33–46	150	40–45

† Data in this table were compiled from: Juračić (1987); Boldrin, *et al.* (1987); Prohić and Juračić (1989); Biščan *et al.* (1991); Cauwet (1991);
[1] Samples collected at Station 1, Figure 1B; [2] Sediment samples collected off the river mouth, Stations 4 and 5, Figure 1B; [3] Samples collected at Station 1 (above the waterfalls), Figure 1C; [4] Estuarine sediments collected at Stations 2 and 3 (in the Prokljan Basin), Figure 1C.

indicates a rather high concentration of trace metals in the suspended matter particles of both rivers compared with the average for marine sediments in the Adriatic Sea. The complexity of physicochemical processes is reflected in comparison between the two rivers and between suspended and sedimented material. For the Adige river the prodelta sediments show increased or at least similar concentrations of trace metals compared to suspended matter. Exactly the opposite is true for the Krka River. Direct comparison shows that zinc and chromium concentrations in suspended matter are similar for both rivers; lead, copper and nickel are at higher concentrations in the Krka river suspended matter, almost three times so for the latter two. Data for the dissolved trace metal concentrations (as far as they are available) indicate that the greater part of these is transported by particulates.

DISCUSSION

The results presented in this paper support the hypothesis that the suspended matter is a key factor determining the assimilative capacity for trace metals (Pb, Cu, Ni etc.). It is the main vehicle for the transport of heavy metals from terrestrial sources to the sea. The assessment of the assimilative capacity of the receiving water body requires a substantial knowledge of the biogeochemical processes involving particulate matter, heavy metals, and organic materials. This assessment also requires a delineation and knowledge of the characteristics of the area to which the concept of assimilative capacity is applied.

The estuaries considered here are contaminated by heavy metals adsorbed on riverine suspended matter. Data are available for the dissolved trace metal concentrations in the Adige River (Cu: 43 nM; Cr 5.9 nM; Cd: 0.6 nN; Boldrin *et al.*, 1989), and in the Krka River (Cu: 1.8 nM; Cd: 0.04 nM; Pb: 0.08 nM; Elbaz-Poulichet *et al.*, 1991), and the calculated dissolved transport index (DTI) (*i.e.* the % of the total metal present in dissolved form) support the assumption that heavy metals are bound to suspended matter. In the Adige River the DTI is 18 for Cu, 34 for Cd and 0.9 for Cr; in the Krka River the DTI is 20 for Cu and 15 for Pb. Recent estimates (GESAMP, 1987) of DTI values for the global gross river flux (Cu: 0.73; Cd: 2.4; Pb: 0.15) are lower than measured in these rivers, apparently a consequence of the different quality and amount of organic material in suspended particulate matter. The larger DTI values indicate anthropogenic souces of contamination with these metals. The very low concentration of suspended matter in the Krka River renders this contamination relatively insignificant.

The behaviour of these trace metals also depends on geochemical processes in the estuarine mixing zone. These processes can lead either to the retention in the mixing zone by sedimentation, or to remobilization into the dissolved state and transport to the open sea (Salomons and Foerstner, 1984). The mixing zone parameters are the salinity gradients, pH change, and the exchange between particulate and dissolved organics, both riverine and marine.

The waters of the Adige river have a high pH of 7.8, but are less well buffered due to the geochemical nature of clays and acid volcanic rocks in the drainage area, and therefore prone to be acidified by atmospheric fall-out and terrestrial run-off. The concentration of the particulate organic matter is low, but there are no data on dissolved organic materials. However, most dissolved organic species are coagulated in water of high salinity, and scavenging due to adsorption and chelation of most trace metals occurs. In the Adige River, the observed high concentration of trace metals in the prodelta sediments, compared with the lower concentration in suspended matter particles, indicate that the dissolved trace metals in the mixing zone are adsorbed on particulates and then removed from the water column by sedimentation.

The waters of the Krka River are buffered by the high concentrations of calcium and magnesium carbonates, keeping the pH high, 7.8 (Biščan *et al.* 1991). The high concentration of particulate organic matter in river water is correlated with the high concentration of trace metals in suspended matter. The sediments have a much lower organic content, and this correlates well with the lower concentration of trace metals. The only obvious mechanism is the chemical or biological degradation of the riverine particulate organic matter. In the Krka River estuary the much lower concentration of trace metals in the prodelta sediments, compared with the concentrations in the suspended matter, indicate the prevailing desorption and dissolution of metals in the mixing zone. Thus processes of desorption and dissolution of trace metals predominate, and influence a larger marine area. The concentrations and total amounts are low and do not present an immediate threat of pollution. However, the inorganic mineral particulates carried in the river flow are deposited mainly within the estuary.

These conclusions are of a general nature, although specific metals can show a different behaviour, *e.g.* copper and cadmium dissolution in the Adige River mouth (Boldrin *et al.*, 1989).

The comparison of the geochemical fate of heavy metals in the two river mouths definitively demonstrates the importance of particulate matter for the assessment of the total assimilative capacity of the region. However, in the Adige river prodelta the capacity is limited by the "tolerable" loading of the prodelta sediments, based on the water and sediment quality criteria. The assimilative capacity of the open waters of the Adriatic Sea is not affected.

In the Krka River estuary, the mobilization of heavy metals by desorption and solubilization is contaminating the open Adriatic waters of a broader area, whereas it does not pollute the inner estuarine zone.

Thus, the concept of the assimilative capacity, and accordingly a decision which and how many activities can be located in an area, requires detailed scientific knowledge of such biogeochemical processes.

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