Integrated modelling of eutrophication and organic contaminant fate in rivers

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Abstract Eutrophication and contamination by toxic organic pollutants are the major problems in water quality management. Despite the fact that both problems have been subjected to extensive research and modelling, they have traditionally been treated separately. Because the models used are single-issue models, many interactions between nutrient cycles and organic contaminant fate and effect are missed. Linking these models is essential to evaluate the fate and risk of contaminants in aquatic ecosystems subjected to dynamic nutrient and organic contaminant loadings. Using a multi-compartment model (air, water and benthic sediment), and a conceptual dynamic hydraulic model (continuously stirred tank in series), a one-dimensional dynamic integrated model with basic water quality and organic contaminant fate sub-models is developed in this work. The model was evaluated based on the Crocodile River (South Africa) and the river Lambro (Italy) case studies for nutrient dynamics (inorganic nitrogen) and organic contaminant fate (Linear Alkylbenzene Sulfonates, LAS) respectively. The model calibration, validation and the scenario analysis results are presented. The results show that the interaction of nutrient dynamics and contaminant fate and effect should be considered in the exposure assessment of river ecosystem. Furthermore, the integrated model gives more valuable information for various scenario analyses than single-issue models.
Keywords Bioaccumulation; exposure modeling; river water quality

Introduction

Eutrophication and contamination by toxic organic pollutants are the main problems in water quality management. Despite the fact that both problems have been subjected to several studies, they have been treated as separate issue and their interaction is missed. This is based on the assumptions that the change in the trophic status has a negligible feedback on toxicant fate, and the toxicity produces a negligible feedback on physicochemical processes that determine the toxicant fate (Koelman *et al.*, 2001).

The interaction between eutrophication and contaminant fate may occur via many mechanisms. Eutrophication may cause dilution of contaminants by increasing amounts of microbial biomass, enhancing biodegradation in the presence of oxygen, organic contaminant scavenging with suspended particulate organic matter (POC), sedimentation of contaminants and contaminant uptake in the food chain. Organic contaminants may have direct or indirect toxic effect on aquatic organisms, which in turn, affects the organic contaminant fate and nutrient cycles (Legovic, 1997). As single-issue models do not address these interactions, an integrated model of eutrophication and organic contaminant fate is required.

The aim of this study is to refine an integrated model of eutrophication and organic contaminant fate in rivers, in which the interaction of nutrient dynamics and organic contaminant fate and effect can be investigated on the basis of time series. Using a multi-compartment model (air, water and benthic sediment), and a conceptual dynamic hydraulic model (continuously stirred tank in series model, Beck and Reda, 1994), a one-dimensional dynamic integrated model with a basic water quality submodel (on the basis of the IWA River Water Quality Model No.1, RWQM1, Reichert *et al.*, 2001) and an organic contaminant fate model is developed. The application of the model was evaluated based on the Crocodile River (South Africa) and the river Lambro (Italy) case studies for nutrient dynamics and organic contaminant fate (Linear Alkylbenzene Sulfonates, LAS) respectively. The importance of the model is presented based on the field data and some scenario analysis.

Model Formulation

Eutrophication model

As a single-issue model, the eutrophication model is concerned with the fate of algae (phytoplankton) and green plants and in its implications for the dissolved oxygen concentration and the nutrient cycle. The most widespread eutrophication model in rivers is QUAL2 (Brown and Barnwell, 1986) type model, which however has many limitations as presented in Reichert *et al.* (2001). Thus, the IWA Task group on River Water Quality Modelling proposed River Water Quality Model No.1, RWQM1 (Reichert *et al.*, 2001). This model has an extended eutrophication model that includes nutrient cycle and simplified food chain model, and can be extended towards an integrated eutrophication and organic contaminant fate and effect model because of some of its advantages: Both mass and elemental balances are included; though the current version of the model describes a simple food chain in which only one group of algae (as producer) and one group of primary consumers (as herbivores) are considered, it can be extended to a more complex food chain model by describing the main subgroups of producers and consumers. Once an appropriate food chain model is formulated, bioaccumulation in the food chain model and toxicity can also be integrated. In this study, the interaction of nutrient dynamics and the simple food chain up to primary consumers are taken into account in order to demonstrate the usefulness of this approach rather than pursuing completeness of the model.

As the RWQM1 model is a relatively complex eutrophication model, and requires large input data sets, a simplification of some process description and an appropriate submodel selection is undertaken. The procedure for sub-model selection has been presented elsewhere (Vanrolleghem *et al.*, 2001). Nitrification was modeled as a single step process; pH was assumed not to change significantly during the process; stoichiometric coefficients were determined using a simple standard mass composition for organic substances considering the elements C, H, O, N and P; and the conversion rates for the bulk water compartment were formulated with Monod-type limitation factors (Reichert *et al.*, 2001). Benthic sediment is also considered as state variable, and its behavior is described by a single biofilm model. In the biofilm model, two kinetic relations are used: Half order kinetics with multi-substrate limitation (Rauch *et al.*, 1999) for the dissolved oxygen, and first order kinetics with mono-substrate limitation model (Melcer *et al.*, 1995) for the other substrates. The choice was made based on the simplicity of the model implementation in an integrated model and the possibility to compute without much numerical problems. The interaction of the two compartments, the bulk water and the benthic sediment, is described by the governing process equations: Diffusion, sedimentation, and resuspension. These processes are also considered in the contaminant fate submodel (see Figure 1).

Organic contaminant fate model

As a single-issue model, organic contaminant fate models describe the fate and distribution of contaminants in the aquatic system. *EXAMS* (Burns and Cline, 1985) is a well known example of such type of model. A distinction should be made between steady state and dynamic exposure or organic contaminant fate models. The dynamic exposure model takes temporal variations of the toxicant's fate into account, whereas the steady state model assumes no temporal variation and can only be applicable during dry weather flow when the temporal variability of river flow is negligible. As toxicity depends on the duration and frequency of exposure (Reinert *et al.*, 2002), it is only by a dynamic exposure model that the violation of the duration and frequency of exposure in the receiving water can be described. Subsequently, the proposed dynamic organic contaminant fate model was formulated on the basis of a simple dynamic mass balance approach. In this model, the "three phases partitioning" is incorporated in both bulk water and benthic sediment compartments i.e. the partitioning of the contaminant between Particulate Organic Carbon (POC), Dissolved Organic Carbon (DOC) and Truly Dissolved (TD). The model assumes local sorption equilibrium within the compartments, and no equilibrium between the compartments (water, sediment, air, and biota). Other dominant processes included in the model are volatilization, biodegradation (both in bulk water and in benthic sediment), sedimentation, resuspension and diffusion. As some organic contaminants like LAS can degrade by heterotrophic biomass only when there is dissolved oxygen in the system, oxygen limitation is considered in the biodegradation submodel. The effect of toxicity on the abundance of biotic compartments is not considered in the present version of the model. A schematic overview of the model is given in Figure 1. Details of mathematical formulation are presented in Deksissa *et al*. (2003).

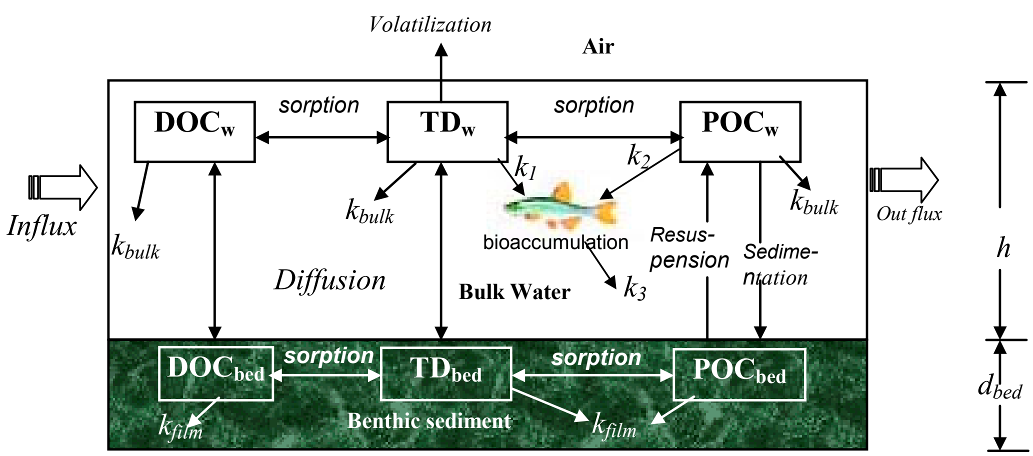

Figure 1 Schematic illustration of contaminant fate and transport model with bioaccumulation submodel in rivers: *h* and d_{bed} are the depth of bulk water and active sediment layer (benthic sediment), respectively; k_{bulk} and k_{film} are the pseudo 1st order biodegradation coefficient in the bulk water and benthic sediment respectively; the subscripts *w* and *bed* indicate the bulk water and the benthic sediment compartment, respectively; k_1, k_2, and k_3 are the bioaccumulation submodel parameters (see equation 1 and 2)

Bioaccumulation in the food chain

Bioaccumulation in the food chain is a governing process in toxic effects where the concentration of the contaminant in a river is very low. In that case, including a bioaccumulation model in the integrated model of eutrophication and contaminant fate is very important. A bioaccumulation model describes the process of contaminant uptake, excretion, and transformation in aquatic organisms and contaminant transfers through aquatic food chains. One of the models that can be applied for non- steady state exposure is a toxicokinetic model, which has been used successfully in pharmacology and allows to predict the toxicant accumulation, distribution, and ultimate effects

(Landrum *et al.*, 1992). A distinction should be made between the simple one compartment model and the multi-compartment models (Mackay *et al.*, 1992; Mancini, 1993). The single compartment model is widely applied because multi-compartment models require many important parameters to be measured or estimated, and for some, this is really difficult. The one compartment model in the bulk water can be expressed as follows:

$$\frac{dM_b}{dt} = k_1 F_w \rho_b M_w - k_3 M_b \tag{1}$$

$$\frac{dM_b}{dt} = \left[k_1 F_W M_W + k_2 F_f C_{POC}\right]\rho_b - k_3 M_b \tag{2}$$

where M_b is the mass of toxicant in the biota (g), k_1 is the contaminant uptake rate from the truly dissolved phase (m^3/g.d), ρ_b is the density of biota in water, M_w the mass of contaminant in water (g), C_{POC} is the sorbed contaminant concentration in the suspended POC (g/g), k_2 is the ingestion rate of the organism (g POC/(g biota. d)), k_3 is the elimination rate (1/d), and F_w and F_f are the water uptake rate efficiency and the contaminant assimilation efficiency. In equation (1), only bioconcentration by respiring water is considered, whereas in equation (2), the accumulation of contaminants not only through respiring water but also feeding on sediments or particulates is considered. The difference between the two equations is that the contaminant exposure through food is not considered in equation (1) even though it can be important (Carbonell *et al.*, 2000). In this study, both equations were applied to simulate the contaminant concentration in the biota (small fishes as a primary consumer).

Integrated modelling

The integrated model is formulated by combining the three submodels: Eutrophication, contaminant fate and bioaccumulation in the food chain. The submodels are linked with the following processes as indicated by Koelman *et al.* (2001) as well:

1. Organic carbon cycle in water column and sediment and the association of contaminants with organic matters POC and DOC.
2. Transport and accumulation of toxic substance in the food chain.
3. Toxicity of contaminants and impacts upon the structure and functioning of the components in the food chain.
4. ‘Bottom’ up versus
5. ‘Top down’ control of the food chain structure by nutrients levels and fluxes.

With the exception of process number 3, the other interactions can be addressed by combining eutrophication, contaminant fate and bioaccumulation in the food chain submodels. Besides, both POC and DOC are considered as state variables. The contaminant sorption to bacteria is also included in the POC. The model was implemented in the modeling and simulation environment WEST® (Vanhooren *et al.*, 2003) and the state variables of all three submodels were calculated simultaneously.

Study Sites

The study is based on the Crocodile River (South Africa) and the Lambro River (Italy). The Crocodile River is situated in the Mpumalanga Province in the north east of the Republic of South Africa (see Figure 2, left). It is a relatively large river basin with a total main-stem river length of approximately 320 km draining a catchment area of about 10,450 km^2 (DWAF, 1995). In this study, consideration was focused on the 153 km long central section of the river, between Montrose weir (upper point) and Krugerwildtuin (lower point), as this is the section that is under greatest water quality problems (Deksissa *et al.*, 2003). In the Lambro River, the study section is between Mulino de Baggero (as upstream point), and Biassono (as downstream point) with a total length of about 26 km (Figure 2, right). The most relevant pollutant discharge is from the wastewater treatment plant (WWTP) effluent in Merone, and the combined sewer overflows (CSOs) with a pollution equivalent of 118,200 inhabitants.

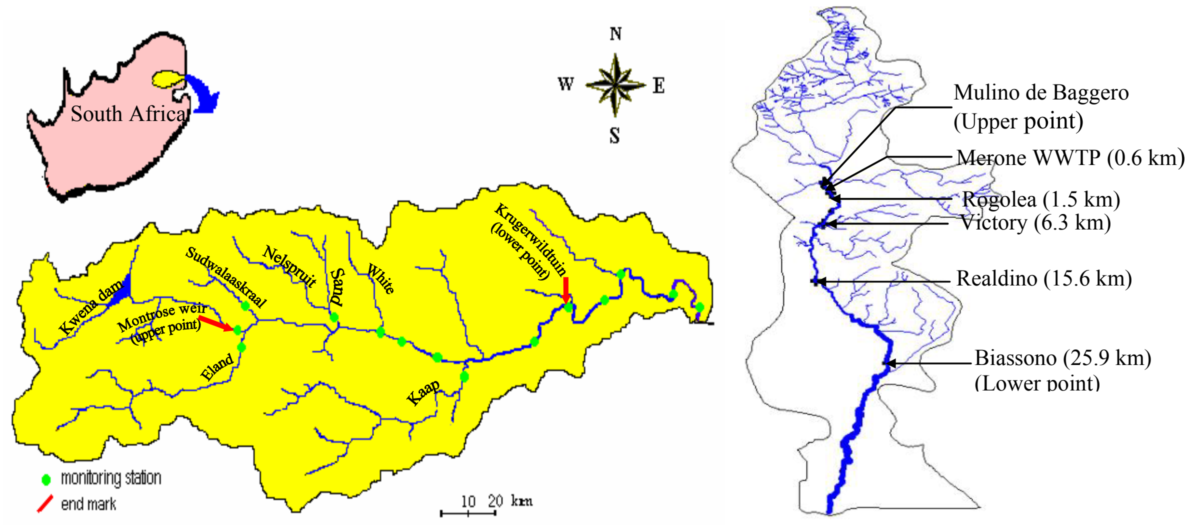

Figure 2 Crocodile River basin (left) and the Lambro River basin (right)

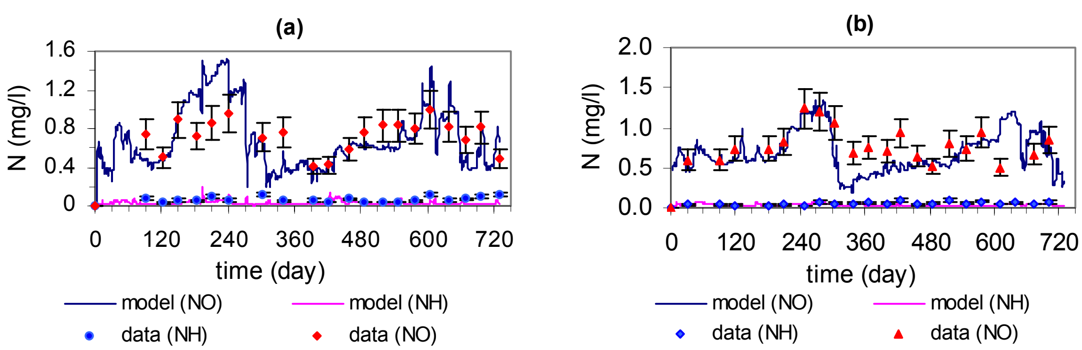

Figure 3 Model calibration (a) and model validation (b) for nutrient dynamics: ammonia (NH) and nitrate plus nitrite (NO) at 153 km (lower end)

Results and discussion

Model calibration and validation

As it is very difficult to get reliable and complete monitoring data for all submodels, the eutrophication and organic contaminant fate submodel were evaluated on different river systems. The eutrophication model was evaluated on the basis of four years monitoring data (1987-1991) of the Crocodile River (South Africa) case study. The model was calibrated for the first two years and validated with the next two years data (Deksissa *et al*., 2003). The result shows that the simulated data set agree well with the measured data set despite the limited set of monitoring data (see Figure 3).

In the Crocodile River, the concentration of ammonia nitrogen is very low throughout the studied years. Nitrate nitrogen concentration shows seasonal dynamics, high during dry seasons and low during wet seasons. This is due to the diluting effect of the river flow during the wet season. The high fresh water withdrawal during critical low flow conditions in the upstream river section, especially in the arid and semiarid regions, is very important for the water quality management (Deksissa *et al.*, 2003).

The organic contaminant fate model was calibrated and validated (Deksissa *et al*., 2003) on the basis of monitoring data collected in the Lmbro river in view of the GREAT-ER project in February and May 1998 respectively (Whelan *et al.*, 1999). The result shows that the simulated data set agrees well with the measured data set (see Figure 4).

Scenario analysis

The interaction of nutrient dynamics and contaminant fate can be further illustrated with scenario analyses. Four different scenarios are considered. Using equations (1) and (2) and kinetic parameters given in Tolls *et al*. (2000), and *Giri et al.* (2000), the tissue concentration of LAS is used to evaluate the importance of the interactions between nutrient and organic contaminants in the river Lambro. The first scenario concerns the effect of limiting nutrients (e.g. ammonia nitrogen) on the bioaccumulation of LAS in a primary consumer (small fish). The results show that the increase of ammonia nitrogen concentration in an oligotrophic river system (0.057 –5 mg/l NH-N) decreases the LAS tissue concentration (see Figure 5, left). This is due to the fact that increasing the limiting nutrient level enhances microbial growth (algal bloom and bacterial growth) and thus increases the POC concentration. Biodegradation and sorption to POC decreases the contaminant concentration in the water, and consequently decreases the bioavailable contaminant concentration.

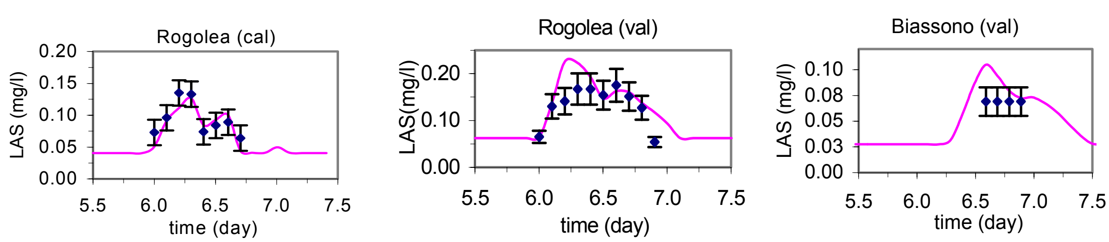

Figure 4 Model calibration (cal) and validation (val) for total LAS concentration in the bulk water at the monitoring stations of Rogolea (1.5 km) and Bissono (26 km)

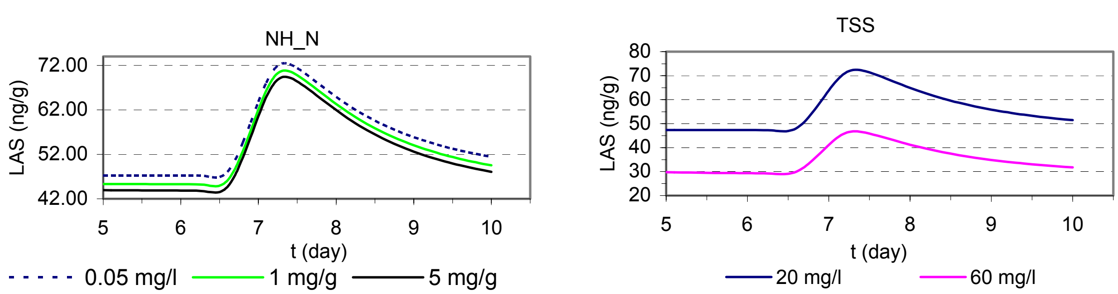

Figure 5 The effect of ammonia nitrogen (NH_N) and total suspended solid (TSS) dynamics on the tissue concentration of LAS in the river Lambro

In the second scenario, a high nutrient load and an increased total suspended solid concentration were considered. The results show that the increase of TSS increases the scavenging of LAS by sorption to POC, and then enhances the removal of LAS by sedimentation (see Figure 5, right). Increasing of TSS from 20 to 60 mg/l results in a significant difference in the tissue concentration.

In the third scenario, the effect of physicochemical characteristics of the contaminant *Kp*, i.e. the organic carbon -water partition coefficient was investigated. The *Kp* values of LAS homologues vary from 220 to 9000 l/kg and this range is used for this scenario analysis. The results show that there is no difference in the tissue concentration for *Kp* values of 220 –1000 l/kg (see Figure 6, left). However, the *Kp* value of 9000 l/kg can decrease the LAS concentration in tissue. This indicates that a higher *Kp* means that a higher contaminant mass is sorbed to POC and less contaminant is available for bioconcentration. Note that the organism can also get the sorbed contaminant via feeding on POC but then the assimilation efficiency governs the rate of bioaccumulation. The assimilation efficiency for toxic contaminants is generally very low (Mackay, 2000).

The fourth scenario is related to the frequency of higher contaminant load, which often associated with a combined sewer overflow (CSO). As the LAS concentration in the treated wastewater treatment plant effluent is very low, the main cause for a high contaminant concentration is usually due to combined sewer overflows (CSO). In many high rainfall regions, the contamination events due to CSO are frequent. Dia-Fierros *et al.* (2002) presented even daily CSO contamination in Spain. Subsequently, the pulse frequency of two and four day's interval of CSO contamination was investigated. Considering the same amount of mass loaded in every pulse (knowing that the total mass loaded within the given time is higher in the higher frequency than the lower frequency), the results show that the higher frequency of CSO contamination results in a higher, progressive increase of the tissue concentration (see Figure 6, right). This is due to the fact that there is less recovery time for the organism to reduce the tissue concentration by excretion or biotransformation.

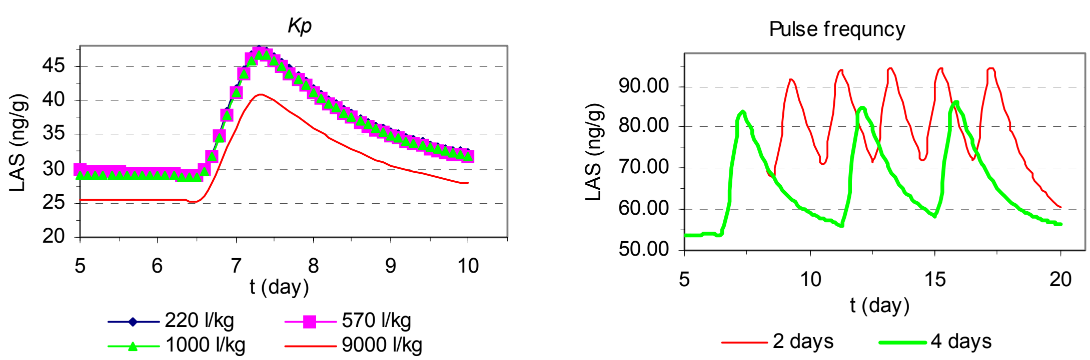

Figure 6 The effect of the partition coecfficient Kp and the frequency of CSO contamination on the tissue concentration of LAS in the river Lambro

Conclusions

An integrated model that includes an eutrophication submodel (RWQM1) and an organic contaminant fate and transport submodel in rivers is formulated on the basis of simple dynamic mass balance approach. The model assumes completely mixed tank in series and local sorption equilibrium within the compartments. However, it assumes no equilibrium between the compartments (water, sediment, air, and biota). Besides, the model takes both special and temporal variability into account. Based on the case studies and scenario analysis the following general conclusion can be drawn:

1. The proposed model comprises a dynamic exposure model and relatively complex eutrophication model, and hence can be very useful for various scenario analyses.
2. Linking bioaccumulation submodel with eutrophication and organic contaminant fate submodels gives more valuable information than just a single-issue model because it considers the interaction of different factors.
3. As eutrophication can have a dilution effect on contamination, the interaction of nutrient dynamics and contaminant fate and effect should be considered in the exposure assessment.
4. The proposed model is sufficiently complex to be applied for short time simulation (daily) of contaminant fate, nutrient cycle and bioaccumulation in the river ecosystem.
5. The results of case studies and scenario analysis show the usefulness of the model in integrated river water quality management.

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