

## **Risk assessment of urban runoff pollution in rivers : how to deal with time-varying concentrations ?**

Evaluation du risque des rejets urbains dans les rivières: comment évaluer les concentrations variant dans le temps?

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### **RESUME**

Les polluants contenus dans les eaux de ruissellement provenant des zones urbaines se retrouvent dans les eaux de surface où ils peuvent engendrer des effets sur les organismes qui y vivent. Les concentrations de ces substances dans les eaux varient beaucoup, les maximums étant atteints lors des événements pluvieux. Dans ce travail, nous proposons un concept basé sur deux critères pour évaluer le risque pour l'environnement aquatique de cette pollution dynamique. Le premier critère est fixé en fonction du temps et protège les organismes contre les pics de pollution ; le second critère protège les organismes à long-terme. Ces critères ont été calculés pour différents paramètres mesurés dans les eaux pluviales: herbicides, matière en suspension, température, ammoniac.

### **ABSTRACT**

The pollutants carried by urban stormwater runoff usually end in surface water and may induce deleterious effects on aquatic organisms. The concentrations of these substances in water are highly variable and the maximum are generally reached during rain events. In this study, we propose a concept based on two criteria to assess the aquatic risk of this highly dynamic pollution. The first criterion is time-dependent and protects the organisms against pollution occurring in pulses; the second criterion protects the organisms on a long-term basis. These criteria were determined for different parameters measured in stormwater runoff: herbicides, total suspended solids, temperature, ammonia.

### **MOTS CLES**

Risk assessment, sustainable river management, time-dependent water quality criteria, urban runoff.

## 1 INTRODUCTION

Rainwater runoff from urbanized areas has in the recent years received increasing attention from the public and scientific community, because it is perceived to induce deleterious effects on the aquatic biota. Indeed, several studies have shown that a wide variety of pollutants are present in rainwater runoff, mainly resulting from the wash-off of the surfaces (Burton and Pitt 2002). For example, heavy metals emitted from traffic are commonly detected in rainwater runoff, but also pesticides (Revitt et al. 2002) or biocides used in building material (Burkhardt et al. 2005). In a separate sewer system, this pollution often ends in rivers without any treatment and consequently impacts on aquatic life are expected. It is therefore crucial to assess the risk of rainwater runoff pollution.

Environmental risk assessment is commonly done by comparing measured environmental concentrations with water quality criteria set to protect the aquatic life for a long period of time (European Commission 2003). However, these long-term criteria are not suitable to estimate the effects of the highly dynamic pollution resulting from wet-weather discharge. Indeed, the contaminants reach surface waters directly through surface runoff during rain events and occur at maximum concentrations just after reaching the water body. This exposure pattern results in time-varying and repeated contamination of the aquatic system. Very little is known about the effects of short but high peaks of exposure. Standard laboratory toxicity tests usually used to assess the effects of pollutants utilize continuous exposure scenarios and typically do not investigate the toxicity of short-term pulsed or intermittent exposures to aquatic organisms. In fact, the necessity in assessing the effects of such high concentration events has been discussed by several authors (Brent and Herricks 1999; Reinert et al. 2002; Diamond et al. 2006). In theory, *in situ* methods would provide the most realistic estimation of actual exposure conditions (Jurgensen and Hoagland 1990). However, it is very difficult to distinguish *in situ* between the effects of the substance of interest (for example a heavy metal) and the effects of parameters that also vary during rain events such as change in temperature, in nutrient concentration, effects of other chemicals, etc.... Recently, Brent and Herricks (1999) proposed a laboratory-based toxicity testing and analysis protocol that can provide more realistic estimates of acute toxicity for wet weather events. They also consider long-term effects (post-exposure effects) of these events. This approach is interesting but based on whole effluent testing. The effects induced by the samples are thus specific to the sample composition, which can vary from one rain event to another. These results are therefore difficult to extrapolate and use in the risk assessment of rainwater pollution in general.

In our laboratory, we recently developed a new testing procedure that allows estimating the effects of time-varying concentrations of some pollutants (Vallotton et al. 2006). The aim was to add a third variable to the classical concentration-response curve used to predict the effects of a substance on an organism, namely the exposure duration. We obtained thus a three dimensional graph expressing the effects of a given substance function of the exposure duration and concentration, which can be compared with the dynamic concentrations of this substance in surface water. These concentration-exposure duration-response curves can also be used to determine time-dependent water quality criteria (Chèvre et al. 2006). Until now, we determined such curves for some herbicides commonly found in rainwater discharges (Vallotton et al. 2006; Vallotton et al. submitted). Based on literature data, we also established these curves for total suspended solids (TSS; Rossi et al. accepted), for temperature (Rossi and Hari submitted) and for ammonia (Rauch et al. 2002, Krejci et al. 2004).

## 2 MATERIAL AND METHODS

### 2.1 Pulse toxicity testing of herbicides

In our laboratory, we developed a method to estimate the effects of time-varying concentrations by focusing on two herbicides regularly detected in pulses in surface water: the triazine atrazine and the phenylurea isoproturon. They are both inhibitors of the photosynthesis, but belong to different chemical classes. Both herbicides have a main agricultural source, but triazines and phenylurea are regularly detected in urban runoff (Hoffman et al. 2000; Revitt et al. 2002).

We assessed the effects of herbicides on the algae *Scenedesmus vacuolatus* cultivated in laboratory for years (Valotton et al. submitted). Algae cultures were inoculated and the herbicides added after 24 hours (Figure 1). This delay in chemical addition was necessary to reach a higher algal density and thereby enabling assessment of the effects of short exposures. The algae cell density was measured four times to enable the calculation of the growth rate during the first ten hours. For longer exposure duration, the cell density was measured 3 times a day as in the standard test. For each exposure duration (10h to 48h), we estimated the concentration that inhibits 50% of the growth ( $EC_{50}$ ) compared to unexposed algae. This value is represented function of exposure duration in the results.

The recovery or a post-exposure of the algae (Figure 1) was studied for exposure duration not exceeding 24 hours, to make sure algae grow exponentially in the controls throughout the experiment. To remove the chemical, the algae cultures were centrifuged 7 min at 3000 rpm at 25°C. The supernatant was discarded and the algae re-suspended in fresh media. The centrifugation was repeated a second time ensuring 99.9% isoproturon and atrazine removal. Controls were handled the same manner. This procedure was tested on unexposed algae culture to ensure that centrifugation does not impair algal growth. During recovery, the growth and the photosynthetic activity were measured as described previously.

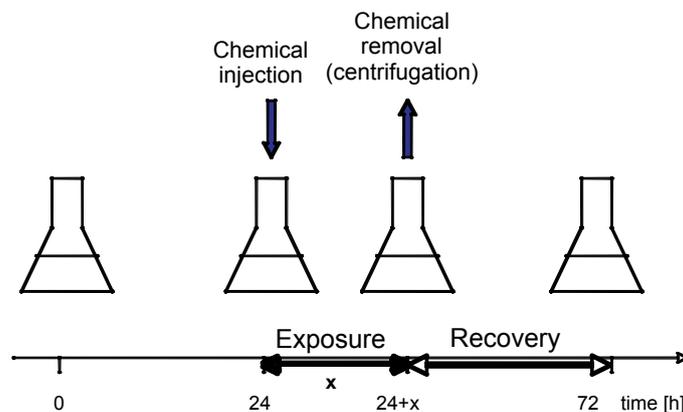


Figure 1 : Exposure protocol for the assessment of pulse exposure and the subsequent recovery. The cell density is regularly measured with a cell counter during the experiment.

Short summary of each method to define the time-dependent toxicity of the other stressors (TSS, temperature, ammonia) will be presented later together with the results.

### 3 RESULTS AND DISCUSSION

#### 3.1 Pulse toxicity of herbicides

##### 3.1.1 Time-dependent toxicity of atrazine and isoproturon

Figure 2 describes the time-dependent toxicity of atrazine and isoproturon on the alga *S. vacuolatus*. The toxicity of both PSII inhibitors increases with exposure duration. The  $EC_{50}$  of atrazine decreases from factor of about 3 between 10 hours and 48h exposure. The decrease occurs mainly during the first 24 hours. The  $EC_{50}$  of isoproturon also falls with increasing exposure durations but to a lesser degree, i.e. from a factor 1.5. Even if both compounds target the same site on PSII, their time-dependent toxicity revealed different toxicodynamics and an isoproturon pulse is prone to induce greater effect on growth in the environment.

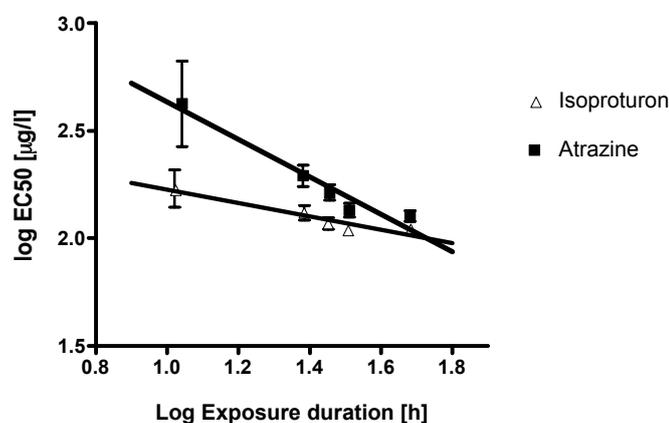


Figure 2: Time-dependent toxicity of atrazine and isoproturon.

Furthermore, our experiments show a systematic growth recovery of the algae during the post-exposure period following exposures lasting 10 to 24 hours and for concentrations up to 300 µg/l for atrazine and isoproturon (Vallotton et al. submitted). These observations can be linked with the rapid recovery observed at the photosystem II level. Indeed the inhibition at the target site on photosystem II decreases quickly to zero (no inhibition) as soon as the herbicide is removed from the algae medium (Figure not shown, see Vallotton et al. submitted). We could therefore conclude that both compounds have a reversible mode of action after a single pulse exposure.

##### 3.1.2 Time-dependent water quality criteria for herbicides

Based on these experiments, we propose a concept for time-dependent water quality criteria (Figure 3). The criteria is divided in two parts: part A accounts for short events (typically rain event) and the criteria varies with event duration; part B accounts for longer occurrence of pollutants and is equivalent to the classical chronic water quality criteria proposed in legislation of several countries (see for example Nowell and

Resek 1994; Roussel 1999; Zabel and Cole 1999). This criterion corresponds to a threshold concentration above which we can expect long-term effects of the substances. We are currently studying the definition of such criteria for atrazine and isoproturon (based on the above results), as well as for metolachlor, another herbicide commonly detected in surface water.

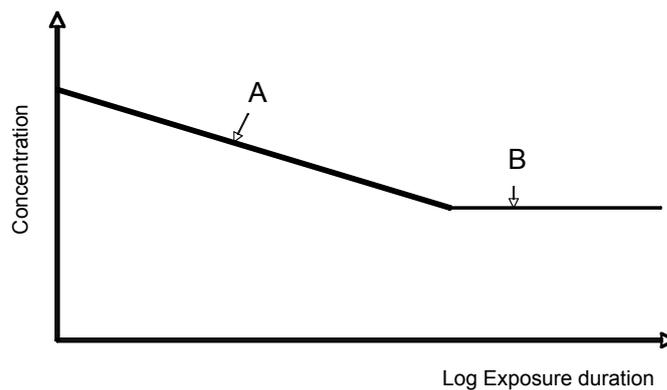


Figure 3: Proposed concept for time-dependent water quality criteria

## 3.2 Time-dependent water quality criteria for other stressors

We also determined time-dependent water quality criteria for other stressors than herbicides also occurring in pulses in receiving water, namely total suspended solids (TSS), temperature and ammonia. The methods to determine these criteria have been published elsewhere and will not be explained in details in this paper.

### 3.2.1 Total suspended solids (TSS)

Figure 4 presents time-dependent criteria for TSS in receiving water. These criteria account for effects of TSS on fishes based on laboratory experiments. This criteria is lowered by a safety factor to also consider the effects of pollutants that can be adsorbed to TSS (for examples PAHs, heavy metals, etc.; Rossi et al. accepted).

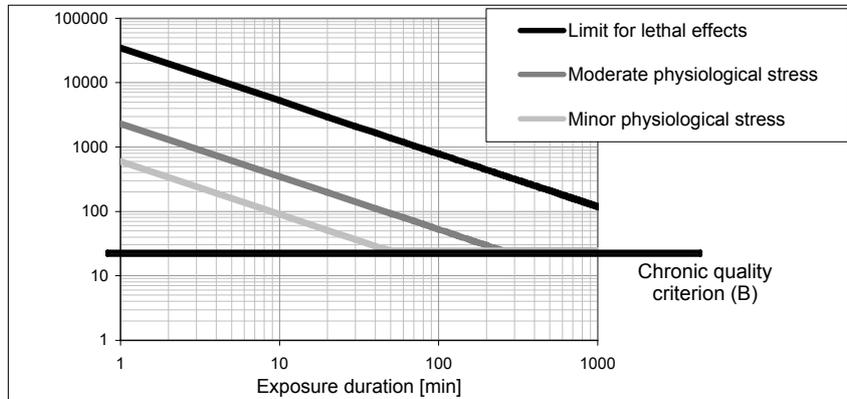


Figure 4: Time-dependent criteria of total suspended solids (TSS) to protect fishes. The water criteria are defined for minor, major and lethal stress (figure adapted from Rossi et al. accepted).

### 3.2.2 Temperature

Rossi et al. (2004) have recently proposed a time-dependent water quality criteria for temperature in rivers (Figure 5). Indeed, the discharge of urban stormwater during a rain event in summer can induce a short temperature elevation in receiving waters that can affect the aquatic organisms. The criteria have been defined based on laboratory studies on salmonidae (Chinook salmon and brown trout; Armour 1991; Elliott 2000) and should protect these sensitive species during summer stormwater events.

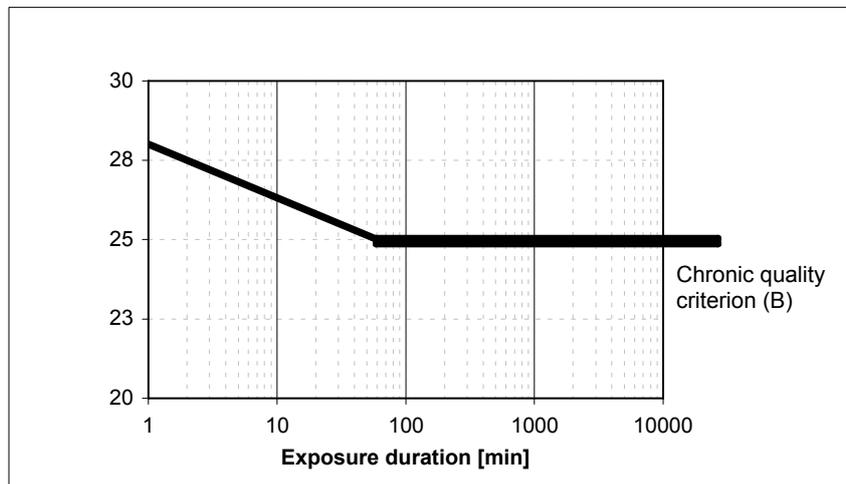


Figure 5: Time-dependent water quality criteria for temperature to protect fishes. This criteria account for different acclimatization temperatures of the fishes (figure adapted from Rossi and Hari submitted).

### 3.2.3 Ammonia

Rauch et al. (2002) proposed a time-dependent water quality criteria for ammonia in surface water (Figure 6). The criteria express a 10% lethal effect on fishes (based on laboratory experiments) and should therefore not be exceeded to avoid deleterious effects on these species.

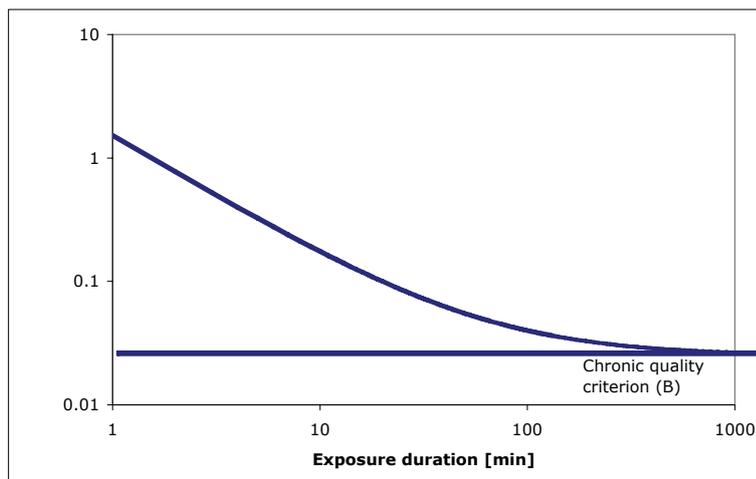


Figure 6: Time-dependent water quality criteria for ammonia to protect fishes (figure adapted from Rauch et al. 2002).

## 4 CONCLUSION AND OUTLOOK

In this paper, we presented several time-dependent water quality criteria, which can be used for pulse concentrations resulting from rain events. This approach may be extended to other compounds (for example heavy metals, see Diamond et al. 2006). The critical point, however, is to determine which concentration has to be compared with the time-dependent criteria. In our opinion, not only the maximum concentration and its duration should be compared with the criterion, but also for example the average concentration with its duration. This would allow a better effect assessment of the event. Furthermore, with the proposed criteria, we do not consider the effects of multiple pulses and recovery period. These parameters are not easy to include in criteria. Indeed, first results with algae show that the rapidity and the completeness of the recovery depend on the chemical studied, mainly its mode of action. However, Diamond et al. (2006) suggest that the effects of pulsed exposure at the sublethal level are more likely if the concentrations approach the species acute threshold and if multiple pulses occur within a short period of time. Modelling (see Watanabe et al. 2005; Ashauer et al. 2006) may be helpful to also account for multiple pulses in regulation.

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