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Investigating the relationship between toxicity and organic sum-parameters in kraft mill effluents

Catherine E. Raptis[*], *Ronnie Juraske*, *Stefanie Hellweg*

Chair of Ecological Systems Design, Institute of Environmental Engineering, ETH Zurich, Zurich 8093, Switzerland

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ABSTRACT

Elaborate toxicity diagnostics, such as toxicity identification evaluation (TIE) and effects-directed analysis (EDA) have helped in identifying the causative agents of effluent wastewater toxicity. However, simpler means of relating ecotoxicological effects to effluent composition could be useful for effluent management practices when there is no scope for more complex procedures. The aim of this work was to investigate and isolate the relationship between biological responses and commonly measured organic sum-parameters, such as chemical- and biochemical oxygen demand (COD and BOD, respectively) in kraft mill effluents. In a top-down approach, the whole effluent toxicity (WET) of effluent samples was first determined from *Pseudokirchneriella subcapitata* and *Ceriodaphnia dubia* bioassays. The theoretical toxicity that could be attributed to the metal content was then estimated, via a combination of equilibrium chemical speciation- and metal toxicity modelling. By assuming concentration addition, the metal toxicity was subtracted from the WET, isolating the toxicity thought to be caused by the organics. Strong and significant correlations between the 'corrected' toxicity and organic sum-parameters were found for both species. The growth of *P. subcapitata* was negatively associated with increasing COD concentrations, whereas reproduction of *C. dubia* was negatively associated with increasing BOD concentrations. The linear relationships, along with robust estimations of their uncertainty bounds, can provide valuable, albeit rough, guidance for kraft mill effluent management practices.

1. Introduction

The attempt to elucidate the causative agents of aquatic toxicity in the complex chemical mixtures presented by effluent wastewater, whether municipal or industrial, is far from new. Procedures such as toxicity identification evaluation (TIE) and effects-directed analysis (EDA) have aided in diagnosing the source of toxicity (Burgess et al., 2013). Nonetheless, the purposes of wastewater effluent management might also be well served if simpler, less involved means of relating observed ecotoxicological effects to effluent composition could be achieved. To this end, it appears reasonable to try to uncover the relationship, if any, between traditional, commonly monitored measures of bulk organic content and biological responses. Whole effluent toxicity (WET) tests reveal whole organism responses to effluents, taking into account all substances and their interactions (Chapman, 2000; Mount and Mount, 2013), and with endpoints of survival, growth and reproduction, the protection they offer extends to

* *Corresponding author*. Tel.: +41 44 633 61 08.
E-mail address: raptis@ifu.baug.ethz.ch (C.E. Raptis).
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the population level (Chapman, 2007). Sum-parameters such as total organic carbon (TOC), chemical oxygen demand (COD) and biological oxygen demand (BOD) are widespread indicators of the quality of effluents, so, relating these values to WET test responses, particularly in effluents where the impacts can be largely traced back to organic chemicals, could provide some valuable support in effluent management practices.

Results from previous such attempts have varied. Research into mixed treated industrial effluents has revealed significant correlations between acute toxicity and COD, in one case involving mixed effluent from 52 industrial plants and *Vibrio fischeri*, and in another 135 industrial plants and *Daphnia pulex* (Araújo et al., 2005; Sánchez-Meza et al., 2007). At the same time, poor or no correlations have been reported after attempts to jointly associate separate WET test results and measures of organic content from distinct treated effluent streams pertaining to a multitude of industrial plants (from different sectors). This does not come as a surprise, given the greatly differing nature of treated effluent compositions, and hence the actual mix of substances behind measures such as TOC (Manusadžianas et al., 2003; OSPAR Commission, 2007).

Several researchers have drawn attention to the complementarity of chemical measurements and ecotoxicological tests (Huybrechts et al., 2014; Mendonça et al., 2009; Vasquez and Fatta-Kassinos, 2013), especially in cases where it is shown that organic content levels below the given regulatory limit do not necessarily guarantee the absence of toxicity – itself an important result (Gómez et al., 2001; Ra et al., 2007). However, in adopting local legislative measures/limits in analyses with WET results (Teodorović et al., 2009), a systematic attempt to investigate the relationship between toxicity and monitored sum-parameters tends to be overlooked. The necessary systematic approach to such an investigation is also absent in studies where the sample size is too small (Hernando et al., 2005). There is a trade-off between completeness of effluent analysis and practicality in its management, and in that respect, while not advocating the cessation of parallel WET tests, any significant established relationship between ecotoxicity and organic sum-parameters (the latter measured on a daily/frequent basis), would certainly afford useful guidance in periods between the less frequent WET tests. It is worth pointing out that in seeking a relationship between WET test results and organic sum-parameters, only effluents that have undergone secondary treatment are considered, since concern is focused on the point of discharge into the aquatic environment. In fact, there have been instances where a reduction of organic content through secondary treatment has not equated with a reduction in toxicity (Köhler et al., 2006; Sánchez-Meza et al., 2007), which could be due to biodegradation products exhibiting higher toxicity compared to their parent compounds (Farré et al., 2008). Whatever the effect of the given secondary treatment is, with a strong established link between the toxicity and the concentration of organic sum-parameters at the end of the treatment line, environmental management purposes can be served by adjusting the process line to ensure that the impact on aquatic biota of the final discharge is controlled.

Pulp and paper mill effluents have long been scrutinised for their impacts on aquatic biota (Hewitt, 2011). Assuming a kraft pulp mill with relatively little variability in terms of raw materials, processes and wastewater treatment, it might not be entirely unreasonable to expect that the bulk organic matter explains, to some extent, any observed ecotoxicological effects. In fact, a statistically significant negative correlation was recently shown to exist between fish reproduction (eggs per female) and BOD concentration in biologically treated kraft mill effluents from seven distinct Canadian mills, suggesting that the control of this sum-parameter could make an informed contribution to best management practices (Kovacs et al., 2011). Motivated by this finding, the goal of this work is to investigate the association between WET test results and organic sum-parameters obtained in a comprehensive and long-term study of kraft mill effluents. The data gathered by the National Council for Air and Stream Improvement (NCASI) in their long term receiving water study (LTRWS) (Hall et al., 2009) present a unique opportunity to investigate the relationship between toxicity and bulk organic content in treated kraft mill effluents. Based on the mixture toxicity concept of concentration addition (Norwood et al., 2003; Sprague, 1970), assumed valid for the organic chemicals and the metals as groups, this work aims to examine whether subtracting the theoretical total toxicity due to the metal content from the whole effluent toxicity isolates and improves the relationship under investigation.

2. Materials and methods

2.1. The data

All data come from the NCASI LTRWS, which includes, among others, one of the most comprehensive and long-term (>10 years) studies of kraft mill effluent quality, in terms of chemical analyses and bioassays. The data consist of unprocessed WET test results and accompanying effluent chemistry analyses [including organic sum-parameters (TOC, COD, BOD), metals, cations, pH etc.], relating to four bleached and unbleached kraft mills, which, between them, process hardwood, softwood, and recovered fibre, and all of which employ state-of-the-art biological treatment. Further details can be found in (Hall et al., 2009).

2.2. WET bioassay analysis and toxicity estimation

The short-term chronic WET bioassay results from effluent samples for *Ceriodaphnia dubia* and *Pseudokirchneriella subcapitata* (formerly known as *Selenastrum capricornutum*), obtained during the LTRWS according to standard methods (USEPA, 2002), were analysed via regression-based model fitting. This is an improved bioassay result analysis approach compared to others, such as the linear interpolation method (Norberg-King, 1993; USEPA, 2002), insofar as it ensures a reasonable fit through suitable parameterisation (deterministic part) and accounts for the type of response via an appropriate error structure (stochastic part), depending on the type of response measured (Ritz and Van der Vliet, 2009). The deterministic part for both species was the 3-parameter log-