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### PULP AND PAPER MILL EFFLUENTS: OBSERVED REPRODUCTIVE EFFECTS ON FISH AND POTENTIAL CAUSAL AGENTS

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#### Introduction

A wide range of alterations in fish endocrine and reproductive systems have been consistently associated to exposure to pulp and paper mill effluents<sup>1</sup>. However, after 20 years of first evidences, there is still discussion on which are the causal agents <sup>2-4</sup>. This work is designed to review the biological effects reported in different fish species in relation to industrial process characteristics, improvements achieved by specific process modifications, and evidences of the suspected causal agents.

#### **Methods and Materials**

We reviewed published work on endocrine disruption effects of pulp and paper mill plants, including field and laboratory exposure experiments, together with available data on production and waste treatment processes, effluent characteristics, and bioaccumulation of marker compounds (e.g. chlorophenolics).

#### **Results and Discussion**

A wide range of reproductive effects have been reported in fish as a consequence of exposure to pulp and paper mill effluents, namely, reduced gonad weight, disfunction in steroid synthesis and metabolism, decreased plasma steroid levels, masculinization (including secondary sex characteristics and behavior), altered sex ratio, reduced egg production and hatchability, delayed sexual maturity, reduced capability of spawn, and increased vitellogenin (VTG) expression. Some of those effects were initially attributed to the presence of persistent organochlorines in the final effluent. However, changes in the bleaching processes, viz. replacement of molecular chlorine to chlorine dioxide, notably reduced the formation of organochlorines, and consequently, the exposure of fish to these compounds; and this was reflected by lower EROD induction in exposed fish. Generally, the potency of those effluents to reduce hormone levels, and gonadosomatic index, decreased. Other effects, such as masculinization of female fish, did notice little change. The observed improvements on water quality and fish health could not be directly linked to a reduction on organochlorines emission, because, changes in the bleaching process were often, undertaken simultaneously to the introduction of effluent secondary treatment or other changes. Hence, mill condensates, which comprises a variety of low molecular weight neutral compounds, and that were shown to reduce sex steroid levels, were efficiently removed by the introduction of reverse osmosis or biological effluent treatments. Plant sterols, e.g. b-sitosterol, are though to contribute to endocrine disruption effects of paper mill effluents. Some observed effects, such as induction of vitellogenin, may be partially explained by the estrogenic effects of b-sitosterol. Pulp and paper mills are also a source of alkylphenol ethoxylate compounds, whose degradation products, e.g. nonylphenol, can contribute to the estrogenic charge of the effluent. Maculinization of

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female fish can not be explained by the mentioned agents, but androstenedione has been detected in river waters in the vicinity of a mill plant using an androgen receptor affinity bioassay, and it has been hypothetically associated to such effects.

Studied species varied on they responsiveness and sensitivity. Perch, roach, mummichog, turbot, goldfish and sunfish showed reduced steroid levels; whereas mosquitofish, channel catfish and killfish suffered from masculinization. Altered sex ratio has only been detected in eelpout, although assessed in a variety of species. Other outcomes, such as increased VTG, have been sporadically assessed, and they can not be attributed to specific species. Additionally, differences on the development and reproductive stages of the studied organisms may affect the reproductive response, and may certainly account for the inconsistent results obtained in different studies.

On a geographical point of view, most of the reproductive impact studies are concentrated in North America, Australia and North Europe, despite France, Italy, Portugal and Spain being within the third and seventh higher producers of cellulose, paper and board of Europe. Although most of these mills have introduced effluent secondary treatment and reduced molecular chlorine in the bleaching processes, southern European rivers are characterized by low flow rates, and consequently lower dilution factors of final effluents can be expected, which will accentuate their potency to cause biological effects. Additionally, species inhabiting southern rivers may have different sensitivity. Since we can not extrapolate results from existing studies, there is an urgent need to investigate the impact of pulp and paper mill effluents in Southern Europe.

In summary, the coexistence of other pollutant sources, the complexity of pulping effluents, the often fragmentary information available in terms of chemical characterization of effluents or reported effects, are key factors that hamper progress in defining reproductive effects and causing agents. Additionally, the multiple pathways by which chemicals can interfere with endocrine system together with species differences in sensitivity add further complexity to the system.

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