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# Vertical distribution of AhR-activating compounds in sediments contaminated by modernized pulp and paper industry

*H. Ratia**, *A. Oikari*

*Biological and Environmental Sciences, University of Jyväskylä, Ambiotica 40014 Finland*

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ABSTRACT

Increased ethoxyresorufin-O-deethylase (EROD) activity is a sensitive biomarker of exposure to the chemicals which activate the aryl hydrocarbon receptor (AhR) and induce the cytochrome P450 system, such as many polychlorinated dibenzo-*p*-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs) and polychlorinated biphenyls (PCBs). Pulp bleaching was one of the main sources of PCDDs and PCDFs until elemental chlorine free (ECF) and total chlorine free bleaching processes since 1990s have remarkably decreased but not completely eliminate discharges of these chemicals. In addition, historically contaminated sediments may act as a source of these persistent contaminants. In this study, the contamination history and recovery of a watercourse heavily loaded by the chemical wood industry were studied by analyzing PCDDs, PCDFs and PCBs from vertical sediment samples and by measuring hepatic EROD activity from rainbow trout intraperitoneally dosed with the sediment extracts. No PCDDs or PCDFs were found above the chromatographic limit of detection from the study area and only small amounts of PCB congeners 101, 138, 153, and 180 were present. No increased EROD activity was observed in fish indicating the absence of any AhR-activating compounds in the surface sediment, to about 15 cm depth, representing about the last 20 years when kraft pulping and ECF bleaching with activated wastewater treatment have been used. It can be concluded that nowadays organochlorines and other AhR-ligands do not harm the previously heavily polluted watercourse.

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## 1. Introduction

The chemical wood industry was long a remarkable source of polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) as by-products of pulp bleaching, similar to polychlorinated biphenyls (PCBs) which were used in manufacturing of carbonless copy paper from the 1950s to the 1970s. PCDDs, PCDFs and PCBs are included on the original list of persistent organic pollutants under the Stockholm Convention, and due to their persistence and toxic characteristics, these chemicals are still widely studied (Owens, 1991; Sundqvist et al., 2009). Since the early 1990s the worldwide pulp and paper industry has mostly used total chlorine free or elemental chlorine free (ECF) bleaching methods. This has largely decreased but not totally eliminated the formation of the PCDDs and PCDFs (Strömberg et al., 1996). Although the deposition of PCDDs and PCDFs to the sediments has decreased since 1980s (Huestis et al., 1997), elevated concentrations in the surface sediments still exist in polluted

* *Corresponding author*. Tel.: +358 440690966.
E-mail address: heli.ratia@jyu.fi (H. Ratia).

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watercourses and coastal areas (Sundqvist et al., 2009). Benthic animals may affect the fate of the chemicals accumulated in the sediments due to bioturbation, migration and trophic transfer (Reynoldson, 1987). Many countries banned the use of PCBs already in the 1970s. However, elevated concentrations of PCBs also are still measured from both terrestrial and aquatic environments (Anon., 2001).

Hepatic ethoxyresorufin-O-deethylase (EROD) is an integrated endpoint to all ligands of aryl hydrocarbon receptor (AhR) activating compounds, which are bioavailable to animals. EROD activity is used as a sensitive biomarker of exposure to the PCDDs and PCDFs and other dioxin-like planar compounds and its increased activity has been detected from fish exposed to pulp and paper mill discharges (van der Oost et al., 2003). Furthermore, some of the PCBs (van der Oost et al., 2003) and polyaromatic hydrocarbons, for instance retene (7-isopropyl-1-methylphenantrene) (Oikari et al., 2002), are known EROD inducers. Retene is transformation product of resin acids (Tavendale et al., 1997) and has been commonly found in the sediments downstream from the pulp and paper mills (Lahdelma and Oikari, 2005). The transition to total chlorine free or elemental chlorine free technologies decreased EROD activity in fish caught downstream from pulp and paper industry (Karels et al., 1999).

In this study PCDDs, PCDFs and PCBs were analyzed from lake sediments contaminated by pulp and paper mills in Fennoscandia from the depths which have deposited after the use of elemental chlorine in bleaching ceased in 1993. The primary aim of the study was to assess the presence of these compounds in the surface sediment layers, i.e. those which could nowadays be exposure sources to fish or benthic invertebrates either by bioturbation or by other disturbances. Burrowing freshwater invertebrates are most abundant in the uppermost 5–10 cm of sediment, for instance chironomids commonly stay in the uppermost 2 cm (Nogaro et al., 2008), whereas oligochaetes may burrow down to 10 cm (Särkkä, 1987). Also other disturbances, like heavy floods or runoffs may increase the water flow and hence the sediment remobilization and bioaccessibility of the chemicals present there (Stachel et al., 2004). Accordingly, the aim of this study was to include all the AhR-ligands present in the given sediment by injecting sediment extract intraperitoneally into the fish body, followed by EROD activity measurement as a response. The null hypothesis was that nowadays the uppermost sediment layers of studied watercourse should not contain AhR-activating compounds.

## 2. Materials and methods

### 2.1. Study sites

The study area is located downstream from the pulp and paper industry in Äänekoski City, in Central Finland. In 1899, a board mill was established, followed by paper and saw industries shortly thereafter. The first chemical pulp mill was introduced in 1938, producing sulfite cellulose and chlorine-based bleaching was started in the 1950s. The kraft mill started in 1961 and a new board mill in 1966. Untreated wastewaters of the mills were discharged to the watercourse until the 1970s when the mechanical treatment began. However, the watercourse did not start to recover before 1985, when both old pulp mills were closed and a new kraft mill with activated wastewater treatment was initiated. In 1993, ECF bleaching process using chloride dioxide and oxygen delignification were introduced. Finally, in 1999, pulp washing and oxygen delignification were further improved resulting in 30% decrease of chemical oxygen demand by wastewaters. The paper and board mills had their own wastewater treatment plant using chemical and mechanical methods. In 2011, the production capacity of the board mill and ECF bleached pulp was 240,000 and 520,000 tons per year, respectively. Paper production was ceased at the end of 2011.

For comparison, Southern Lake Saimaa in South-East Finland was used as a potential positive reference as previous studies on fishes conducted there have shown induced EROD activity (Karels et al., 1999; Oikari et al., 2002). Moreover, pulp and paper mills discharging to Southern Lake Saimaa, have quite a similar history as the mills in Äänekoski (Lahdelma and Oikari, 2005).

### 2.2. Sediment sampling

Sediment samples were taken from Lake Vatianjärvi and Lake Leppävesi, 15 and 33 km downstream from pulp and paper mills in Äänekoski, respectively (Fig. 1). The watercourse collects its inflows from two sources: relatively humic water from the Saarijärvi-Naarajärvi route and oligotrophic water from the Viitasaari-Keitele route. The reference site is located in oligotrophic Lake Keitele, 16 km upstream from the mills.

Samples were taken by Limnos device in late October 2011 during the turnover which occurs annually in autumn and spring in most boreal lakes. Therefore, the water temperature (7 °C) and oxygen concentration (11–13 mg/l) were similar in the water surface and near the sediment in every sampling site. Sediment profiles were sectioned to 2 cm slices in the field and stored in cooled boxes during the sampling. For the bioassay, 3–5 replicates were combined to the glass jars and stored in the dark at 4 °C until extracted and used in the bioassay, within two months. For chemical analysis of chlorinated compounds, one sample (approximately 150 g) was placed to the separate 1.5 dl glass jars and kept in the dark at 4 °C before being freeze dried for analyses of PCDDs, PCDFs and PCBs.

Surface sediment (0–10 cm) taken by an Ekman device from Southern Lake Saimaa was the positive control (Fig. 1). Southern Lake Saimaa sediment is known to induce hepatic EROD activity in rainbow trout (Oikari et al., 2002). Rautniemi sediment from Southern Lake Saimaa and Lake Keitele sediment were the pristine references, and were also taken by an Ekman device in 2011 (Fig. 1).

### 2.3. Sediment analyses

Loss on ignition (LOI), considered as an approximation of the organic carbon, was determined from the dry sediments (SFS, 1990) (550 °C, 2 h). Thereafter, the obtained results were normalized to LOI as it is known that AhR-ligands as hydrophobic xenobiotics associate with the organic part of the sediments (Delle Site, 2001).

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