

The compounds 2,4-dichlorophenol (2,4-DCP) and 2,4-dichloro-6-nitrophenol (6-nitro-2,4-DCP) have been detected at $\mu\text{g L}^{-1}$ levels (10^{-9} - 10^{-8} M) during the summer season 2005 in the water of the Rhône river delta. Compound 2,4-DCP would mainly derive from the transformation of the herbicide dichlorprop, heavily used in flooded rice farming (1400 kg in the delta region in 2005), in addition to being an impurity of the commercial herbicide. Field data show a fast concentration decrease of 2,4-DCP in the period June 21st to July 5th, accompanied by a corresponding increase of 6-nitro-2,4-DCP. This could imply a possible nitration process of 2,4-DCP into 6-nitro-2,4-DCP, with quite elevated yield (33%). Nitration of 2,4-DCP can be induced by photoproducted $\bullet\text{NO}_2$, the reaction kinetics (calculated in the presence of Fe(III) + nitrite under irradiation as model system) being $d[6\text{-nitro-2,4-DCP}]/dt = 650 [2,4\text{-DCP}] [\bullet\text{NO}_2]$. Interestingly, the yield of the process (38%) is similar to that suggested by field data. An indirect assessment of $[\bullet\text{NO}_2]$ in surface water in different sites of the Rhône delta indicated that 2,4-DCP could be transformed into 6-nitro-2,4-DCP in a couple of weeks or less in the shallow water (10 cm depth) of the rice fields, a time scale that is compatible with field data. Photonitration of 2,4-DCP is thus a possible process to account for the occurrence of 6-nitro-2,4-DCP in the Rhône delta.