

# Occurrence of Fungicide Oxadixyl In the Surface Water of an Urban Lake

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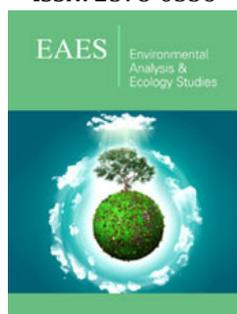
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## Abstract

Banning of the Oxadixyl fungicide started year 2003 in France, but after 8 years, our study clearly gave an evidence that it can be detected in the surface water of Bordeaux Lac, France. Oxadixyl can pose harm to human and aquatic resources especially when toxicity is the issue. Two water sampling campaigns were performed in 2011, in four different locations of the lake. Concentration detected were from less than 2ng/L to a maximum of as 160ng/L. The collector of rain waters displays some important concentration measured and can be considered as a source, but not the only one. This is as highest concentration during the 2nd sampling campaign was detected almost at the center of the lake in 6 meter deep. Also, the presence of this molecule in most of the sampling duration despite differing meteorological conditions indicates its persistence. The results instigate the necessity to further monitor Oxadixyl in the area to pinpoint the sources. Furthermore, although the concentration seems low, mass fluxes should be looked into. Mostly, if environmental risk and management are to be considered.

**Keywords:** Oxadixyl, Emerging contaminant, Surface waters, Persistent pollutant, Aquatic system

## Introduction

Oxadixyl (C<sub>14</sub>H<sub>18</sub>N<sub>2</sub>O<sub>4</sub>) is a phenylamide fungicide [1]. This fungicide is used to treat diseases caused by Oomycetes family [2]. It was employed since 1986 for various purposes such as protection of barley, potatoes and vegetables (Lettuce, Carrot, Cabbage, Spinach, etc.), treatment of ornamental tree seeds and treatment of the soils. In Southwest of France, it was specifically used against mildew, a common disease seen in the vineyards. The use of Oxadixyl in France was prohibited since year 2003 as it was found toxic for the environment and for humans. According to the European Regulation of 1907/2006/EC, Article 31, Oxadixyl is toxic to aquatic life with long lasting effect. For humans, it is harmful if swallowed and inhaled, and in contact with skin and eyes.

As a systemic pesticide, it implies environmental distresses. Systemic pesticide persists in soil for long duration that reaches groundwater, resulting to contamination [3]. Another type of risk in water is that Oxadixyl slowly hydrolyzes that can release ammonia and form acetate salts [4]. In the United States, product cancellation was earlier as it started year 2002. The aim of this study is to find out if Oxadixyl is present in the surface water of Bordeaux Lac in France. This lake is important for its recreational use (swimming area and sailing school) and habitat for aquatic resources. Lakes are prone to organic contamination [5] due mostly to different agricultural [6] and industrial activities [7]. The occurrence of organic molecule in aquatic systems should be assessed to determine the state of the water quality [8]. Sampling campaigns were done in 2011, 8 years after the banning was implemented.

## Site background

Bordeaux Lac is situated in Southwest of France, Northern part of Bordeaux City. It is manmade, used to be a swamp area, dug during 1960 with a surface area of 150ha. Its depth can extend to around 15m deep. Water comes from the local water table. This lake is a

home to aquatic species such as lacustrine and cyprinids. It caters recreational activities such as fishing, swimming every summer, and nautical service such as sailing school. This lake accommodates surface water runoff channeled by a collector. Climate of Bordeaux area is temperate, with oceanic influence. Monthly average temperature ranges from 6.6°C in January to 21.4 °C in July (measures from 1981 to 2018). Annual accumulated rainfall is approximately 950mm.

## Method

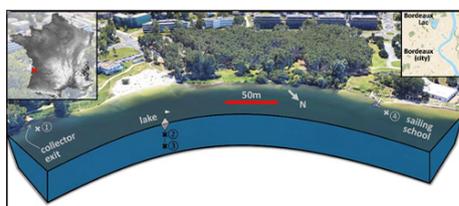
### Sampling sites

Four (4) sampling sites were chosen (Erreur! Source du renvoi introuvable.gure 1). Sampling site 1 is at the collector, discharging

**Table 1:** Accumulated rainfall before the sampling dates.

Accumulated rainfall	First Sampling Campaign			Second Sampling Campaign		
	20-Jun	27-Jun	04-Jul	12-Aug	19-Aug	26-Aug
3 days before	6.2	0	0	0	0.4	27
7 days before	7.2	0.8	0	2.4	3.6	27.2
10 days before campaign	9.6			16		
20 days before campaign	19.6			30.8		

This season is considered as a dry period. Before the second sampling campaign, a long rainfall period started on the 7<sup>th</sup> of July with a peak on mid-July (Figure 1). The months of July and August gave rainfall records that are higher than the monthly normal average. Although, the year 2011, was considered a dry year, these months succeeded in having rainfall above the normal monthly average. Thus, this season can be considered as a wet period.



**Figure 1:** Bordeaux Lac Sampling Sites (Image modified from Google Map).

Using the conventional method, collecting water samples was done manually. Each amber bottle was immersed to the water and then immediately covered with a cap (to avoid airborne contaminants). There should be no air bubbles, so it has to be checked. If there is, the procedure should be repeated. Van Dorn water sampler is used for collecting waters with specific depth at the Bordeaux Lac (1 and 6 meters). Water samples were sent to the Laboratoire Départemental d'Analyse et de Recherche de Dordogne (LDAR 24). These were analyzed using the protocol PS 13/14/11 of the Liquid Chromatography Mass Spectrometry (LC-MS/MS).

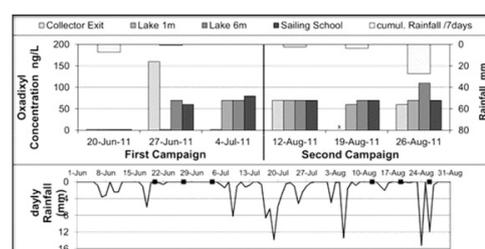
## Result and Discussion

The measured concentration of Oxadixyl in the four sites during the two campaigns is presented in Figure 2. Accumulated rainfall (over 7 days) and daily rainfall are also showed. Eight years after its

surface runoff on urban area (mainly the nearby highway) directly to the lake. Sampling sites 2 and 3 were collected approximately at the center of the lake with 1m and 6m depths, respectively. Sampling Site 4 is at the sailing school.

Two sampling campaigns were done in summer 2011: the first is held from 20 June to 4 July, the second is held from 12 August to 26 August. In both cases, samplings are done three times with one-week interval. Two months before the first sampling campaign was done, the months of March and April did not receive the expected rainfall (average rainfall from 1981 to 2018 are 65mm and 78mm respectively). March had 32.4mm while April had 15.7mm. The scarcity of the rainfall continued while the 1<sup>st</sup> sampling period was conducted. Accumulated rainfall before the sampling dates is presented in Table 1.

interdiction of use, Oxadixyl is still present in the aquatic system of Bordeaux Lac. For the first campaign, the concentrations in the four sites were rather low, 43ng/L on the average. Also, the occurrence of Oxadixyl is variable. For example, concentrations were less than 2ng/L for the sampling of 20<sup>th</sup> of June 2011 for the four sites, but it reached 160ng/L at the collector a week later (27<sup>th</sup> of June 2011). During the second campaign, the average concentration was 72ng/L with a maximum of 110ng/L at 6m depth on the 26<sup>th</sup> of August 2011.



**Figure 2:** Detected concentrations of Oxadixyl in Bordeaux Lac; rainfall incidences are shown as background information.

The first campaign is following a dry period. Even if the amount of rainfall was lesser, the presence of Oxadixyl was still detected in Bordeaux Lac. This detection indicates that this fungicide reached the surface water. The collector presents strong variations of concentration within a week (first sampling campaign). Yet, it does not seem to be a major contributor of this molecule. The second sampling campaign took place after a rainy period. During this period, the highest concentration was detected at the area of 6 meter deep. Intensity of rainfall and its impact on surface runoff and soil leaching should be investigated. As a phenylamide, its persistence could be expected to maintain stability in the aquatic environment [9]. The study of Aldana et al. [10] showed that Oxadixyl is mobile

in soil columns and leaching can be highly expected. If this is the case, the stock of Oxadixyl in the soil and its surrounding could be mobilized.

Occurrence of Oxadixyl in Bordeaux Lac water is a concern for the health of the people and its aquatic system's biota. Although the concentrations are low, monitoring of this molecule is needed. The area is used as for a recreational activity (e.g. swimming, fishing). People who use this area have the risk of being exposed to this molecule. Water swallowing might be experienced. The origin and transportation processes of Oxadixyl are still not known.

Soil samplings are needed to better estimate the remaining stocks of Oxadixyl. Also, the role of the collector should be assessed, especially the occurrence of high concentrations. The two campaigns showed a general behavior influenced by the rainfall. However, 20 June 2011 and 26 August measurements have different variations despite of the fact that they are following rain event (6mm on 18 June 2011, 16mm on 24 August 2011). Then, the effects of rain event intensity as well as the humidification state of the soil should be addressed. The first sampling campaign showed that during the dry period (when the precipitation is low), the concentration is low, but a peak or highest concentration was detected at the collector.

While during the wet period, in August the pronounced rainfall was experienced. The concentration of the fungicide can be washed out or diluted. Hence, in general concentration can be expected low. Intensity and frequency of the occurrence of rainfall have impact on the concentration of an element or molecule [11]. The highest concentration in the collector during the 1<sup>st</sup> sampling campaign and at the center of 6-meter-deep during the 2<sup>nd</sup> sampling should be further investigated.

## Conclusion

The two sampling campaigns conducted in Bordeaux Lac in June and August 2011 showed that Oxadixyl is still present in the aquatic system even 8 years after its interdiction. The occurrence of Oxadixyl could pose risks for the aquatic system and for the people using the area. Especially as Bordeaux Lac is used for fishing, sailing and swimming by adults and infants. The measured concentrations in water were variable, ranging from less than 2ng/L to 160ng/L. Even if this concentration is considered low, their detection proves its occurrence in this surface water. Its persistence is observed, albeit, the differing rainfall conditions. Also, its concentration variation founds appealing to measure and assess the mass fluxes. Rainfall seems to be a possible driver of Oxadixyl in terms of concentration variations. Leaching of stocks in the soils could

transfer the pollutant to groundwater and later to Bordeaux Lac. However, the transfer processes are not yet clearly assessed. Therefore, monitoring of Oxadixyl in Bordeaux Lac water should be done to better understand the role of rainfall, groundwater and runoff water.

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