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First report on organochlorine pesticides in water in a highly productive agro-industrial basin of the Central Valley, Chile

Monica Montory [a, *], Javier Ferrer [a], Diego Rivera [b], María Valentina Villouta [a], Joan O. Grimalt [c]

[a] *Laboratory of Hydro-Environmental Biotechnology, Department of Water Resources, School of Agricultural Engineering, University of Concepción, Chile*
[b] *Laboratory of Comparative Policy in Water Resources Management, Department of Water Resources, University of Concepción, Chile*
[c] *Institute of Environmental Assessment and Water Research (IDÆA-CSIC), Barcelona, Spain*

HIGHLIGHTS

- This is the first report on OCPs in water in an agricultural basin of Chile.
- The Ñuble basin is characterized for the production of local and exportation fruits, animals farms and agri-food production.
- The results shows similar trends in comparison with other agricultural basins of the world.
- This study is a baseline for future works on OCPs in Chile.

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ABSTRACT

The Ñuble River flows through an agricultural area in the central zone of Chile in which different types of fruits are grown. The objective of this study was to identify the levels and source of organochlorine pesticides (OCPs) in the surface waters of the Ñuble River. Surface water samples were collected at 10 sampling points and analyzed for 19 organochlorine pesticides during the dry (spring-summer) and wet (autumn-winter) periods of 2013 and 2014. The results revealed that concentrations of total OCPs in surface waters ranged from 0.12 to 26.28 ng/l. Endosulfan and lindane were the main OCPs in the water. The maximum OCP levels were found in the dry period, while significantly lower concentrations were recorded in the wet period. This indicates that patterns of OCPs have varied in the last 10 years as this study found low concentrations of DDT and metabolites but significantly increased concentrations of α-endosulfan. Given the fact that OCPs were withdrawn from agricultural used many years ago, their presence indicates that they may be still in use clandestinely. Findings of significant concentrations of endosulfan and lindane in this study lead to the conclusion that the chemical fallow practices contribute to runoff into the river and surface water infiltration into groundwater. Because no studies have previously measured OCP levels in agricultural basins in Chile, this study is an important contribution to the knowledge of organochlorine contaminants present in surface water in Chile.

1. Introduction

Organochlorine pesticides (OCPs) were the most extensively used insecticides in agriculture for many years. Due to their risk to the environment and their effects on human health and wildlife, OCPs have been banned in developed countries since the mid-70s (Koureas et al., 2016). However, they continue to be of concern due to their persistence in environment and significant potential of bioaccumulation. Studies conducted worldwide have shown that pp 'DDE, which is a principal metabolite of DDT, persists in more than 95% of the general population (Zubero et al., 2015).

Adverse health effects from long-term exposure to OCPs have been extensively studied in the literature, reporting results that indicate a possible link to breast cancer, diabetes, decreased semen quality, spontaneous abortion, and alteration in children's neurodevelopment (Eskenazi et al., 2009).

OCPs are a potential hazard through routes of entry, such as consumption of food contaminated or water contaminated with

* Corresponding author. Vicente Mendez 595, Chillan, Chile.
E-mail address: mmontory@udec.cl (M. Montory).

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pesticides (Mahmoud et al., 2016). A study conducted by Wu et al. (2014) indicates that the presence of OCPs in groundwater Northeastern China is associated with increased risk of cancer among people consuming water contaminated with pesticide residues.

The resistance of OCPs to degradation has been evidenced in water samples from agricultural watersheds in which residues and metabolites have been found several years after their use was banned (Wu et al., 2014; Agarwal et al., 2015; Ali et al., 2016). Once these compounds reach groundwater, their traces remain for several years due to the limited microbial activity in groundwater, as seen in samples obtained from wells in agricultural areas of India (Agarwal et al., 2015), South Asia (Ali et al., 2016), and China (Wu et al., 2014). Vegetables and biota absorb OCP residues from the soil, which affects terrestrial food chains (Montory et al., 2010, 2011, 2012). Studies have reported varying concentrations of metabolites in seasonal vegetables in India (Kumari et al., 2002) and Pakistan (Tariq et al., 2007) as well as in invertebrates inhabiting polluted soils (Hongjian, 2008). Therefore, it is possible to establish a relationship between agricultural activity and the presence of OCPs in both surface and groundwater (Barra et al., 2005; Wu et al., 2014; Agarwal et al., 2015; Ali et al., 2014).

In recent years, agricultural productivity in the Central Valley of Chile has increased compared to previous years (CIREN, 2014). In fact, the agricultural activity of the area (mainly fruit exports) accounted for 2.6% of the gross domestic product in 2013 (CIREN, 2014).

In 2005, the government of Chile conducted a study on persistent organic pollutants (POPs) in the country. This study reported concentrations of these compounds in animal foods, vegetables, and milk in the V and VIII Regions (Central Valley). The most common found pesticides were DDT (0.395 mg/kg) followed by aldrin and dieldrin (0.111 mg/kg), heptachlor (0.097 mg/kg) and hexachlorobenzene, as well as 0.031 mg/kg of Endrin, and 0.053 mg/kg of HCB (CONAMA, 2005). These values are spatially consistent with areas of intensive agricultural activity.

Based on the process of international integration and in order to reduce the harmful global impact of chemicals, Chile has ratified the three conventions that regulate chemicals and hazardous wastes at global level: the International Basel Convention, the Rotterdam Convention, and the Stockholm Convention. This resulted in the prohibition of OCPs (MMA, 2011). Chile has also signed other agreements to foster the protection and enhancement of the environment. The Canada–Chile Agreement on Environmental Cooperation (CCAEC) entered into force in 1997 at the same time as the Canada–Chile Free Trade Agreement. In the 2005–2007 Work Program established under the CCAEC, both countries agreed on a broad range of actions around priority areas such as environment, mainly in aspects of control (MMA, 2011). Actions also included to strengthen the implementation of the Stockholm Convention (OCDE/FAO, 31 2007) and the Environmental Cooperation Agreement with the U.S.A.

Currently, Chile is a member of the Organization for Economic Co-operation and Development (OECD), which has led to the improvement of production standards in different key issues for public health, the environment and the productive activities, such as management and safe handling of hazardous chemicals, e.g. persistent organic pollutants (POPs) and, specifically, pesticides (MMA, 2011). The ratification of international conventions for the development of a National Policy on Chemical Safety along with the design and implementation of specific plans aimed at strengthening institutions with regulatory power are important advances, but many challenges still remain in terms of surveillance and monitoring of hazardous chemicals.

Water is essential to life, for all socio-economic development and for maintaining healthy ecosystems. Therefore, the objective of this study was to determine the levels, frequency and magnitude of OCPs in the agricultural basin of the Ñuble River (36° S), which is located in an agricultural area of the central valley of Chile that concentrates 38% of national agricultural exports (ODEPA, 2014). The Ñuble basin is characterized by a production of fruit for export (blueberries), pine and eucalyptus plantations and intensive animal farming (ODEPA, 2014). There is an intensive use of pesticides in the area so that significant concentrations of these elements may be present in its water, which would constitute a potential risk to the health of the ecosystem and people (Papadakis et al., 2015). Once OCPs are absorbed into agricultural soils, growing vegetation can absorb them though their roots or leaves so that animals are likely to ingest some of these contaminated soils or plants (Kumari et al., 2002; Tariq et al., 2007; Hongjian, 2008).

In comparison with the other Latin American countries, Chile possess a high pesticide use estimated as the mass of active ingredient use in Arable Land & Permanent Crops (12.3 kg ha-1 year-1) (FAO, 2015). In fact, pesticide sales have been increasing not only in Latin America, but also in Asia and Europe (FAO, 2015). In this sense, Chile is similar to China in terms of pesticide use but, unlike Chile, China has abundant information on the OCPs present in rivers and agricultural areas (Zheng et al., 2016). On the contrary, there is no information on OCPs in rivers of agricultural zones in Chile and the existing information is outdated since data date back 10 years (CONAMA, 2005).

Therefore, this study represents the first approach to describe OCP levels in a Chilean agricultural basin. This work provides valuable information for the development and improvement of environmental laws, regulations, policies and practices in accordance with the Stockholm Convention. Furthermore, information provided can be also useful for the development of Chilean environmental regulations in terms of the quality of the secondary water of the Ñuble River since it has not been defined by any previous standard yet.

2. Materials and methods

2.1. Study site

The Ñuble River (Fig. 1) drains a catchment area of 5097 km^2. It has great relevance in the development of recreational activities, ecotourism, and especially agriculture, supplying a network of 1119 irrigation canals that cover an area of 56,208 ha (Ñuble River Monitoring Board, 2013). The basin also supplies drinking water to communities and rural villages, which are grouped into various rural drinking water committees.

The main economic activities in the basin are agriculture and forestry. Agricultural land use in the basin comprises 1279 ha. Fruits and vegetables are largely exported, especially berries. The gross area intended for forestry use covers 7723 ha (ODEPA, 2014).

Samples (in triplicate) were taken in the source of the river and near Chillan (Fig. 1) during the dry (spring-summer, September to March) and wet periods (autumn-winter, April to August) of 2013 and 2014 at every sampling point. Four blank points were considered in the mountain zone; they are free from the anthropogenic impact of the use of pesticides in farming due to their location (Fig. 1). Samples were taken in glass bottles of two sizes: 2 L for the points along the river and 5 L for the blank points. The samples were stored away from light and transported cold (4 °C) until they were analyzed in the laboratory. The number of samples was determined based on the geomorphological characteristics and accessibility to the study site, and weather conditions of the season in which they were collected.

The physicochemical properties of the water samples are showed in the supplementary material (Table S1).