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Presence of the β-triketone herbicide tefuryltrione in drinking water sources and its degradation product in drinking waters

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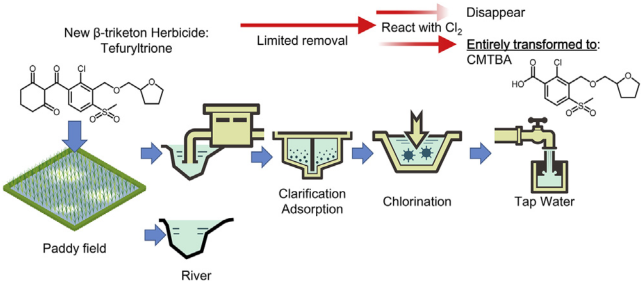
HIGHLIGHTS

- Tefuryltrione, a triketone herbicide, was found in river waters.
- The maximum concentration was 1.85 µg/L.
- In drinking waters, a degradation product (CMTBA) was identified.
- Chlorination transforms tefuryltrione entirely to CMTBA.
- CMTBA in drinking water reached 0.35 µg/L.

GRAPHICAL ABSTRACT



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ABSTRACT

Triketone herbicides are becoming popular because of their herbicidal activity against sulfonylurea-resistant weeds. Among these herbicides, tefuryltrione (TFT) is the first registered herbicide for rice farming, and recently its distribution has grown dramatically. In this study, we developed analytical methods for TFT and its degradation product 2-chloro-4-methylsulfonyl-3-[(tetrahydrofuran-2-yl-methoxy) methyl] benzoic acid (CMTBA). TFT was found frequently in surface waters in rice production areas at concentrations as high as 1.9 µg/L. The maximum observed concentration was lower than but close to 2 µg/L, which is the Japanese reference concentration of ambient water quality for pesticides. However, TFT was not found in any drinking waters even though the source waters were purified by conventional coagulation and filtration processes; this was due to chlorination, which transforms TFT to CMTBA. The conversion rate of TFT to CMBA on chlorination was almost 100%, and CMTBA was stable in the presence of chlorine. Moreover, CMTBA was found in drinking waters sampled from household water taps at a similar concentration to that of TFT in the source water of the water purification plant. Although the acceptable daily intake and the reference concentration of CMTBA are unknown, the highest concentration in drinking water exceeded 0.1 µg/L, which is the maximum allowable concentration for any individual pesticide and its relevant metabolites in the European Union Drinking Directive.

1. Introduction

The annual global consumption of pesticides is estimated to be 24 million tons as active ingredients, and these ingredients represent approximately 900 different chemicals (USEPA, 2011). This

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intentional application of such a huge amount of pesticides to open surface areas may have a strong impact on both the environment and human health. Due to high public concern regarding residual pesticides in drinking water and food, governments restrict authorized concentration in drinking waters through each standard or directive. In drinking water quality standards or directives, however, the degradation products of pesticides are seldom considered. However, some survey studies have reported higher concentrations of degradation products than of original forms in river waters (Hladik et al., 2008; Botta et al., 2009; Iwafune et al., 2010; McMahen et al., 2016).

Rice-farming herbicides easily enter natural river waters at higher rates than other pesticides used in upland farming because they are applied to paddy fields where a large amount of water is irrigated, ponded, and drained during the rice-farming seasons (Narita et al., 2014). According to a national survey of drinking and source water quality (Matsui, 2016), rice-farming herbicides such as molinate and pretilachlor are detected more frequently at high concentrations than other pesticides. The ADI (acceptable daily intake) values of pesticides, which span a broad range (more than five orders of magnitude), affect the significance of measured concentrations relative to the toxicities of pesticides, because the individual guideline values of pesticides are derived from their ADI values.

Given this background information, we focused on a new rice-farming herbicide, tefuryltrione (TFT) (Table 1), and its degradation product. TFT is a β-triketone herbicide, which causes weed whitening and death by inhibiting HPPD (hydroxyphenylpyruvate dioxygenase) activity. Triketone herbicides including TFT are becoming popular, replacing sulfonylurea herbicides, because of their herbicidal activity against resistant weeds (Itoh et al., 1999; Uchino et al., 2000). In Japan, TFT was registered in 2007, and since then has been increasingly used in rice farming. TFT was also registered in 2015 in Korea (Park et al., 2012), and other triketone herbicides (mesotrione, sulcotrione, and tembotrione) are registered in many other countries, including the USA and several European countries (USEPA, 2007, 2009a; ECHA, 2011). Environmental monitoring information about triketone herbicides is gradually accumulating, as is information about their behaviour during water purification processes (Freitas et al., 2008; Patil et al., 2016; Dumas et al., 2017). However, information is still limited regarding their degradation products (Freitas et al., 2004; Durand et al., 2010; Bensalah et al., 2011; Murati et al., 2012; Jović et al., 2013; Barchanska et al., 2016), in particular those found in drinking water.

In an assessment conducted by the Food Safety Commission of Japan (FSC), the ADI of TFT was set at 0.8 μg/kg/day (FSC, 2009), and a prospective reference concentration of 2 μg/L can be derived from this ADI value multiplied by standard body weight (50 kg) and allocation factor (10%), divided by drinking water consumption (2 L). This value is the lowest among the herbicides registered in Japan. Yet, TFT is not included in the list of motoring candidates of the Japanese Drinking Water Quality Guideline (JDWQG) (MHLWJ, 2003), and it is not listed in any of the national drinking water quality standards or guidelines. The low ADI value of TFT, coupled with the recent increase in the quantity of TFT that is shipped annually, raises concern that TFT should be monitored in drinking and source waters.

Accordingly, the aim of this research was to develop a method to analyse TFT in water, to reveal its presence in drinking and source waters, and to investigate its behaviour during the water purification process. Importantly, we identified a degradation product of TFT during the chlorination process, the presence and behaviour of which are also described.

2. Materials and methods

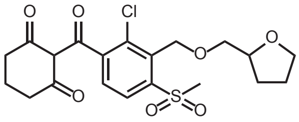
2.1. Sampling points of river waters

Twelve rivers that flow through Kanagawa prefecture were selected for water sampling. Sampling at the Tsurumi River [Fig. S1 in Supplementary Information (SI)] was conducted first and with the highest frequency of every two weeks from April to September 2013 and then April to September 2014. Sampling at the other rivers was conducted every month from April to July 2014. Because high concentrations were detected in the Shibuta River, sampling was conducted every week from May to June 2015. Samples were transported to the laboratory at Kanto Gakuin University for TFT concentration analysis according to the procedure described in section 2.2. In addition to this sampling and analysis, in 2014 and 2015, sampling and analysis were also conducted in 8 prefectures by waterworks authorities (Fig. S2 and Table S1 in SI).

2.2. Analytical method

Because no analytical method for TFT concentration in environmental and drinking waters has yet been reported, we developed one (Fig. S3 in SI) in this study after referring to the analytical method for neonicotinoid pesticides because of their similar low Log-Kow and high water solubility (Kawasaki et al., 2012). After filtrating the sample water through a glass fiber filter with nominal pore size of 1.0 μm (GA-100, Advantec Toyo Kaisha, Ltd.) and adjusting the filtrate to pH 3.0 by adding formic acid (the pH adjustment is less than necessary: it was implemented for the simultaneous analysis of other pesticides), a specified volume (250 mL) of the resultant sample water was passed through an Oasis HLB cartridge (250 mg, Waters Corporation, USA) at a 5 mL/min flow rate by using a concentrator; the Oasis HLB was previously

Table 1
Mass spectrum characteristics of TFT and its degradation product (CMTBA).

	Composition	Theoretical m/z $[M\text{-}NH_4]^+$	Observed m/z $[M\text{-}NH_4]^+$	Δ ppm	MS	MS2	Structure
TFT	$C_{20}H_{27}O_7NClS$	460.1191	460.1194	0.593	460.1194	262.0392 85.0648 305.0479 341.0242	
CMTBA	$C_{14}H_{21}O_6NClS$	366.0773	366.0772	−0.170	366.0774	349.0507 85.0647 246.9823