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Seasonal variation of chloro-s-triazines in the Hartbeespoort Dam catchment, South Africa

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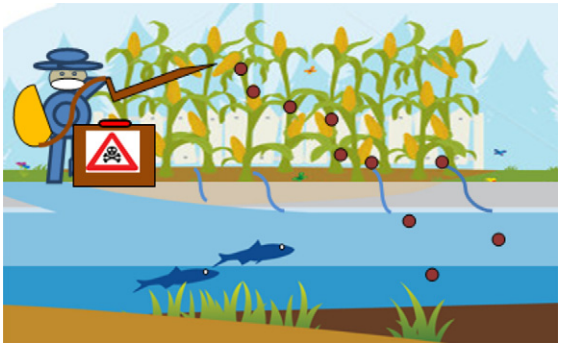
HIGHLIGHTS

- Summer contributed the highest triazine herbicide loads into the Hartbeespoort Dam.
- The Crocodile River is the major source of herbicides in the Hartbeespoort Dam.
- Atrazine groundwater concentrations in the Hartbeespoort Dam proximity are >130 ng L^{-1}.
- DET is the most abundant triazine metabolite in the Hartbeespoort Dam catchment.
- Atrazine metabolites were detected in fish muscle.

GRAPHICAL ABSTRACT



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ABSTRACT

Seasonal variation of eight chloro-s-triazine herbicides and seven major atrazine and terbuthylazine degradation products was monitored in the Hartbeespoort Dam catchment using gas chromatography–mass spectrometry (GC–MS) and liquid chromatography-mass spectrometry (LC-MS/MS). Lake, river and groundwater were sampled from the Hartbeespoort Dam catchment over four seasons and the downstream Jukskei River was monitored during the winter season. Triazine herbicide concentrations in the Hartbeespoort Dam were in the order atrazine > simazine > propazine > ametryn > prometryn throughout the four seasons sampled. Triazine herbicide concentrations in the Hartbeespoort Dam surface water were highest in summer and gradually decreased in successive seasons of autumn, winter and spring. Terbuthylazine was the only triazine herbicide detected at all sampling sites in the Jukskei River, though atrazine recorded much higher concentrations for the N14 and Kyalami sites, with concentrations of 923 and 210 ng L^{-1} respectively, compared to 134 and 74 ng L^{-1} for terbuthylazine. Analytical results in conjunction with river flow data indicate that the Jukskei and Crocodile Rivers contribute the greatest triazine herbicide loads into the Hartbeespoort Dam. No triazine herbicides were detected in the fish muscle tested, showing that bioaccumulation of triazine herbicides is negligible. Atrazine and terbuthylazine metabolites were detected in the fish muscle with deethylatrazine (DEA) being detected in both catfish and carp muscle at low concentrations of 0.2 and 0.3 ng g^{-1}, respectively. Desethylterbuthylazine (DET) was detected only in catfish at a concentration of 0.3 ng g^{-1}. With atrazine herbicide groundwater concentrations being >130 ng L^{-1} for all seasons and groundwater $\sum$ triazine herbicide concentrations ranging between 527 and

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367 ng L^{-1}, triazine compounds in the Hartbeespoort Dam catchment may pose a risk to humans and wildlife in light findings of endocrine and immune disrupting atrazine effects by various researchers.

1. Introduction

The presence of chloro-s-triazines in the environment is predominantly due to herbicide application, particularly from atrazine, simazine, terbuthylazine, ametryn, gesatamin, propazine and prometon (Wackett et al., 2002; Zhang et al., 2016). South Africa is historically the 9th biggest corn producer in the world and atrazine is often used as the herbicide of choice, with 88% of atrazine in the country being applied on corn, though in combination with other triazine herbicides (Dabrowski, 2015; Du Preez et al., 2005). After application, triazine herbicides can seep through soil to contaminate groundwater due to their moderately hydrophilic nature, low K_{ow} and weak soil adsorption (Du Preez et al., 2005; Graymore et al., 2001; Solomon et al., 2008). Atrazine is the most widely used chloro-s-triazine globally and has been detected in various water bodies and groundwater throughout South Africa since the 1980′s (Ansara-Ross et al., 2012; Takáts et al., 2001). Its use is banned in Europe since 2004 due to its relative persistence and risk of water contamination, though the use of the other triazine herbicides is still permitted (Ackerman, 2007; Hang et al., 2005; Herranz et al., 2008; Lin et al., 2011; Omotayo et al., 2011; Wang and Xie, 2012). Atrazine is however still used extensively in China, USA, India, South America, Africa and Australia (Ansara-Ross et al., 2012; Liu et al., 2016; Siddiqua et al., 2010). The maximum allowable limit of atrazine in drinking water in the USA and India is 3 μg L^{-1} (Singh and Cameotra, 2014) whilst the European maximum permissible level of atrazine in drinking water is 0.1 μg L^{-1} (El Sebaï et al., 2011; Herranz et al., 2008; Omotayo et al., 2011).

Triazine herbicide mode of action proceeds by inhibiting photosynthetic electron transport and blocking CO_2 fixation, causing accumulation of CO_2 in the plant, leading to plant death (Wackett et al., 2002; Wiegand et al., 2001). Atrazine is a herbicide of major significance in the Hartbeespoort Dam catchment as it is historically found in the highest concentrations in surface water (Ansara-Ross et al., 2012). In fish, atrazine has been shown to have effects ranging from inhibition of acetylcholinesterase, leading to decreased reflexes, increased respiration (Wiegand et al., 2001) and in addition, it has been discovered to cause a range of adverse effects on the reproductive and immune systems of oral and intravenously exposed rats and frogs (Ross and Filipov, 2006). The effects of ecologically relevant atrazine concentrations on biological species is highly controversial and the scientific community remains divided as there have been inconsistent conclusions drawn by various scientists in different studies, based on different endpoints including growth and gonadal abnormalities (Rohr and McCoy, 2010).

Atrazine has been proven to be an endocrine disruptor in many species (Freeman et al., 2011; Rohr and McCoy, 2010). However, numerous studies of effects of atrazine on the reproductive, nervous and immune systems on humans and animals have produced contradicting results with lack of consistency (Rohr and McCoy, 2010; Solomon et al., 2008; Wirbisky and Freeman, 2017). Atrazine has been observed to cause gene alterations that lead to endocrine disruption in zebrafish, inhibition of ovary growth in crabs, altering sex ratios in crayfish and frogs as well as demusculinising male gonads in fish, amphibians, reptiles and mammals (Hayes et al., 2011; Loughlin et al., 2016; Silveyra et al., 2017; Wirbisky and Freeman, 2017).

1.1. Atrazine and terbuthylazine degradation

Metabolism of atrazine and terbuthylazine is species-specific (Catenacci et al., 1993). In the majority of animals fed with radiolabelled atrazine, the vast majority of atrazine was eliminated unmetabolised, indicating a low bioaccumulation (Solomon et al., 2008). The degradation of triazine herbicides proceeds by microbial, photolytic or non-enzymatic chemical action such as the benzoxazinone catalysed reaction (Lin et al., 2008; Wiegand et al., 2001). This results in dechlorination, deamination or dealkylation, forming a variety of degradation products (Belfroid et al., 1998; Graymore et al., 2001; Loos and Niessner, 1999; Wang and Xie, 2012). The degradation of atrazine in the environment is mainly due to microbial action (Wackett et al., 2002). Atrazine can be metabolized by plants through N-dealkylation primarily by cytochrome P-450 followed by a phase II conjugation reaction to glutathione by glutathione-S-transferase (Ross and Filipov, 2006; Wiegand et al., 2001). Atrazine metabolites have been detected in carp liver of fish exposed to different concentrations of atrazine ranging from 4.28 to 428 μg L^{-1} (Xing et al., 2014) and *in vitro* atrazine exposure tests have shown the presence of monodealkylated deethylatrazine and desisopropylatrazine. Desisopropylatrazine can also be formed by degradation of both atrazine and simazine whilst deethylatrazine can be formed by degradation of atrazine and propazine (Jiang et al., 2005).

Terbuthylazine inhibits photosynthesis by altering chloroplast membrane proteins. Its degradation proceeds primarily either by microbial N-dealkylation of one of the s-triazine side chains to form desethylterbuthylazine (DET) or photolytic hydroxylation and dechlorination of the C2 chlorine to form hydroxyterbuthylazine and desethylhydroxyterbuthylazine (Bottoni et al., 2013; Sanlaville et al., 1996; Velisek et al., 2016). Terbuthylazine is slightly toxic to fish and can also be degraded to desisopropylatrazine and atrazine desethyldesisopropyl which are secondary degradation products arising from terbuthylazine metabolism (Du Preez et al., 2005). This study aims to assess the degree of triazine pollution in the Hartbeespoort Dam catchment and determine the points with the most significant influence triazine pollution for ecological risk profiling. The study design is only indicative of the seasonal variation of triazine herbicides as well as atrazine and terbuthylazine degradation products in the Hartbeespoort Dam catchment area. Though triazine herbicides are still used in South Africa, very little studies have looked at their fate in the environment and biota, particularly triazine metabolites.

2. Materials and methods

2.1. Chemicals and reagents

All analytical standards had a purity ≥96% (Tables 1 & 2) and all solvents had a purity >99.5%. Ultrapure Milli-Q water used in all preparation work was produced by a Millipore Advantage system (Merck, Johannesburg, South Africa) with a total organic carbon <3 mg L^{-1}.

2.2. Study area and sampling

Five sampling sites were located primarily around the major inlets and outlet of the Hartbeespoort Dam (Fig. 1) for determination of the point with the most influence on the Hartbeespoort Dam pollution. Another 5 points were located upstream of the Hartbeespoort Dam, in the Jukskei River where atrazine-use maps, produced by Dabrowski (2015), show significant atrazine use. The GPS coordinates of the Hartbeespoort Dam catchment sampling points are listed in supplementary information (SI) Table S1. The Jukskei River sampling points were sampled in the winter season. They are located downstream of heavily anthropogenically impacted areas further downstream in Johannesburg where the N14, Kyalami, Midrand, Buccleuch and Marlboro sites are located.