Environmental Pollution 219 (2016) 253–261

Contents lists available at ScienceDirect

Environmental Pollution

journal homepage: www.elsevier.com/locate/envpol

# Predictors of pesticide concentrations in freshwater trout – The role of life history☆

Rachel C. Scholes [a, 1], Kimberly J. Hageman [a, *], Gerard P. Closs [b], Claudine H. Stirling [a, c], Malcolm R. Reid [a, c], Rasmus Gabrielsson [b, d], Jason M. Augspurger [b]

[a] Department of Chemistry, University of Otago, Dunedin 9016, New Zealand
[b] Department of Zoology, University of Otago, Dunedin 9016, New Zealand
[c] Centre for Trace Element Analysis, University of Otago, Dunedin 9016, New Zealand
[d] Cawthron Institute, Nelson 7010, New Zealand

ARTICLE INFO

*Article history:*
Received 19 July 2016
Received in revised form
2 October 2016
Accepted 6 October 2016

*Keywords:*
Strontium
Isotopes
Hexachlorobenzene
Chlorpyrifos
Endosulfan
Fish migration

ABSTRACT

Concentrations of halogenated pesticides in freshwater fish can be affected by age, size, trophic position, and exposure history. Exposure history may vary for individual fish caught at a single location due to different life histories, *e.g.* they may have hatched in different tributaries before migrating to a specific lake. We evaluated correlations of pesticide concentrations in freshwater brown trout (*Salmo trutta*) from the Clutha River, New Zealand, with potential predictors including capture site, age, length, trophic level, and life history. Life history was determined from otolith (fish ear bone) strontium isotope signatures, which vary among tributaries in the region of our study. Variability in pesticide concentrations between individual fish was not well explained by capture site, age, length, or trophic level. However, hexachlorobenzene (HCB) and chlorpyrifos concentrations were distinct in lake-based trout with different life histories. Additionally, one of the riverine life histories was associated with relatively high concentrations of total endosulfans. Linear models that included all potential predictor variables were evaluated and the resulting best models for HCB, chlorpyrifos, and total endosulfans included life history. These findings show that in cases where otolith isotope signatures vary geographically, they can be used to help explain contaminant concentration variations in fish caught from a single location.



## 1. Introduction

The concentrations of organic contaminants, especially those that are persistent, bioaccumulative, and/or toxic, are often measured in fish as a way of characterizing the spatial distributions of these contaminants or for monitoring contaminant exposure to humans and wildlife that consume fish (Stewart et al., 2011; Miranda et al., 2008; Singh and Singh, 2008; Xu et al., 2016; Harris et al., 2008). However, contaminant concentrations in individual fish captured at the same site often vary considerably, much more so than is expected for non-biological samples collected from a single site (Daverat et al., 2011). This variability can be attributed to a number of factors that influence contaminant exposure and uptake over the course of an individual fish's life. For example, older fish sometimes have higher contaminant concentrations due to a longer exposure time (Miranda et al., 2008). Furthermore, slower growth and depuration rates can lead to higher contaminant concentrations in larger fish (Gewurtz et al., 2011; Burreau et al., 2006). Additionally, fish from the same location may occupy different trophic positions in their food chain, resulting in different degrees of contaminant biomagnification (Hoekstra et al., 2003).

Another potentially important contributor to the variability in contaminant concentrations in fish is life history. For example, individual fish captured at a single site may have migrated there from different locations and therefore also experienced vastly different contaminant exposures during their lifetimes. Due to the inherent difficulties of tracking fish, many monitoring programs and studies of environmental contamination do not account for this effect, instead focusing only on the catch location of each fish. However, during the last several decades, advances in otolith (fish ear bone)

☆ This paper has been recommended for acceptance by Charles Wong.
* Corresponding author.
*E-mail address:* khageman@chemistry.otago.ac.nz (K.J. Hageman).
[1] Present address: Department of Civil and Environmental Engineering, University of California, Berkeley, California 94720, United States.

http://dx.doi.org/10.1016/j.envpol.2016.10.017
0269-7491/

microchemistry analysis have made it increasingly possible to map fish migrations and stock mixing (Campana et al., 2000) and thus, to determine habitat usage at scales relevant to variations in contaminant exposure. This mapping is possible because calcium carbonate, along with other elements from the surrounding environment, is continuously incorporated onto the exterior surface of the otolith. Trace elements and their isotopes deposited in the otolith provide a continuous signature of the chemical environment experienced over the life history of the fish. For example, diagnostic ratios based on trace element (Olley et al., 2011) and/or metal isotope composition (Daverat et al., 2011; Lochet et al., 2008; Ohji et al., 2007; Le et al., 2010) in otoliths have been used successfully in past studies to distinguish fish life histories. The strontium isotope signature, given by the $^{87}Sr/^{86}Sr$ radiogenic ratio, can be particularly useful as it often varies widely within and between different river catchment systems due to local or regional differences in the underlying geology. Additionally, the $^{87}Sr/^{86}Sr$ signature of otoliths has been shown to exhibit greater stability and resolving power than elemental ratios and stable oxygen isotopes over the lifetime of the fish (Walther and Thorrold, 2009).

The potential impacts of life history on the accumulation of mercury (Lochet et al., 2008), organotin compounds (Ohji et al., 2007), metals (Le et al., 2010), PCBs (Daverat et al., 2011), and metals/PAHs (Dupuy et al., 2015) have previously been investigated in fish and eels using Sr:Ca and Ba:Ca ratios in otoliths. In these previous studies, otolith microchemistry was used to distinguish diadromous (sea-migrating) versus resident freshwater fish. We hypothesize here that differences in life history involved in fish migrations *within* a freshwater system, *e.g.* from different tributaries to a lake or main river, could also result in variable contaminant burdens in fish caught at a single location. This may be especially true when the tributaries flow through areas with markedly different land usages. Thus, the aim of this study was to investigate the relationships between pesticide contaminant concentrations and the life history of individual trout caught in the extensive Clutha River catchment, located on the South Island of New Zealand. Brown trout (*Salmo trutta*) were collected from the catchment at three stream locations adjacent to areas of contrasting land use. A suite of halogenated pesticides was quantified in fish muscle and liver and lifetime trends in $^{87}Sr/^{86}Sr$ signatures measured in otoliths were used to distinguish life histories. Fish capture site, age, length, and trophic level were also included in the analysis as potential predictors of halogenated pesticide concentrations.

## 2. Materials and methods

### 2.1. Sampling sites, collection, and preparation

Adult brown trout were collected via angling from the catchment of the Clutha River (Fig. 1), which is located in the Otago Region and is the largest river on New Zealand's South Island. Fish were collected from three sites: Lake Hawea ($n = 12$), the upper Clutha River ($n = 11$), and the lower Clutha River ($n = 10$). Although spatial pesticide use data is not available in New Zealand, pesticide input via runoff was expected to vary along the river due to differences in surrounding land use. The land immediately surrounding Lake Hawea is largely used for conservation and low intensity grazing and cropping although dairy farms are also present (Hawea Basin Aquifer Draft Information Sheet, 2014). The land surrounding the Upper River site is dominated by vineyards and orchards while the Lower River site is immediately downstream of intensively grazed and cropped land. Three dams restrict the movement of trout between sites (Fig. 1). All fish sampling was completed during the Southern Hemisphere autumn, between 1 March and 15 May 2015. The Clutha River catchment does not receive hatchery-reared trout, nor has it for the last 40 years (Personal communication, 2016); thus, we are confident that all trout were wild born. Directly following capture, fish were sacrificed in accordance with a University of Otago Animal Ethics Committee approved protocol (AEC ET11/15). They were then placed on ice and stored at −20 °C until dissection. Muscle and liver tissue were removed and homogenized with diatomaceous earth (DE) (1:3 homogenate to DE) in a mortar and pestle in preparation for lipid determination and pesticide analysis. Livers of three trout were excluded due to insufficient mass for extraction. Fish length was measured prior to dissection. Saggital otoliths were extracted from each trout and stored dry until further preparation for Sr isotope analysis.

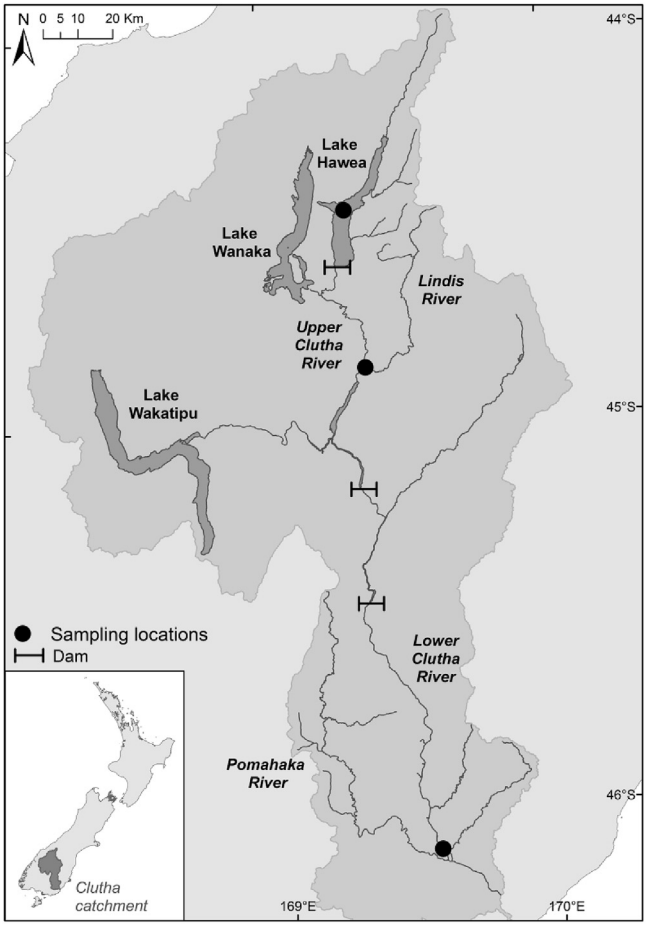


**Fig. 1.** Map of Clutha River catchment, including main tributaries and sampling locations. Black horizontal lines denote the locations of dams.

Water samples were collected from seven water bodies in the Clutha River catchment in 2012 as part of a separate project on isotope signatures in this catchment. Sampling locations included Lake Hawea, Lake Wanaka, Lake Wakatipu, the Upper Clutha River, the Lower Clutha River, the Lindis River, and the Pomahaka River (Fig. 1). At each site, 200 mL ($n = 2–5$) of water was collected during base flow conditions.

### 2.2. Lipid determination

Total extractable lipids were extracted from homogenates using pressurized liquid extraction (PLE) and determined gravimetrically. An aliquot of homogenized sample (5 g of muscle or 2 g of liver) was