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Accidental Discharge of Brodifacoum Baits into a Freshwater Lake: A Case Study

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Abstract Approximately 700 kg of cereal bait containing 20 ppm of the anticoagulant rodenticide brodifacoum was spilled into a southern New Zealand lake in 2010 from a helicopter being used to transport containers of brodifacoum bait for an aerial baiting operation. In the month after the spill no residual brodifacoum was detected in samples of lake water, sediment, benthic invertebrates, eels, and two birds.

Keywords Benthic invertebrates · Brodifacoum · Sediment testing · Water

Brodifacoum is a second-generation anticoagulant rodenticide used for commensal rodent control since the 1970s (British Crop Protection Council 2000). Over the last two decades, broad-scale aerial application of brodifacoum in cereal pellet bait formulations has emerged as an important conservation tool, instrumental in successful eradication of invasive rodents (e.g. *Rattus* spp.) from an increasing number offshore islands (Howald et al. 2007).

On 24 June 2010, a structural failure in a container suspended from a helicopter being used to transport brodifacoum bait for an aerial baiting operation to eradicate rodents from Indian Island, New Zealand, resulted in a spill of bags of Pestoff20R cereal bait pellets. These were multiwall paper bags with polyethylene liner, each containing 25 kg of bait. Twenty-eight bags (700 kg of 20 ppm brodifacoum bait, a total of 14 g of active ingredient) fell into remote Lake Kirirua on Anchor Island in Dusky Sound, southwest Fiordland (lat. −45.7581, long. 166.5340). Some bags ruptured in mid-air or burst on impact with the water; an estimated 18 of the 28 bags were retrieved empty and floating on the lake surface. In a search of the lake and surrounding catchment immediately after the spill, no bait pellets were observed either on the lake surface or on the shoreline, indicating that spillage from the bags had sunk. We assume the other 10 bags sank intact. Because of the remoteness and depth of the lake, recovery of spilled bait was not practicable.

The oral LD_{50} of brodifacoum in *R. norvegicus* has been estimated as 0.26 mg/kg, and the half-life in soil under aerobic conditions as 157 days (World Health Organisation 1995). To examine potential contamination and environmental effects resulting from the spill of brodifacoum, we sampled water, sediment and benthic invertebrates in Lake Kirirua, necropsied two water birds found dead at the time of the sampling, and took liver samples from eels from various parts of the lake for brodifacoum analysis.

Materials and Methods

Lake Kirirua is a glacial remnant of about 30 ha, 23 m above sea level and 10–40 m deep. It has a base of rock and coarse gravel and with no stream inflows is dependent on run-off from a small forest catchment. The low level of sediment is accumulated fine organic material from the catchment, giving the water a tannin stain. The entire lake

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is fringed by mature forest, edged with undercut banks, woody debris and coarse gravel substrate. The lake has a small outfall stream (between 10 and 30 L s^{-1}), so water residence time is probably lengthy. The depth of the lake suggests likely stratification of surface waters from the bottom with little mixing. After the spill on 24 June 2010, we visited Lake Kirirua on 29 June, 8 July and 29–30 July to characterise substrate and water depth, and the fauna present. Fyke- and minnow netting caught long-finned eels (*Anguilla diefenbachii*) around the western lake edge in close proximity to water sampling transects. Other species considered potentially present such as common bully (*Gobiomorphus breviceps*), giant kokopu (*Galaxias argenteus*) or koura (freshwater crayfish, *Paranephrops planifrons*) were not caught by the netting. Benthic invertebrates were sparse, but caddisfly species were present, indicative of an oligotrophic lake of low productivity. A breeding colony of at least 100 pied shags (*Phalacrocorax varius*) was present on the southern embayment near the natural outlet.

Water samples (c. 500 mL, n = 17) were collected 2 days after the spill, at least 30 cm below the water surface at the site where most of the bait bags had entered the lake, and from sites in sheltered arms of the lake, and exposed and well mixed zones. GPS co-ordinates were taken for all water sampling locations. Further water samples (c. 500 mL, n = 10) were taken 2 weeks after the spill using a Van Dorn collector at 1 m above the lake bottom, from where most bait had fallen, where floating bags were collected, and the lake outfall. Two or three samples were also taken at equal intervals along four equally-spaced transects across the length of the lake. All water samples were stored in brown glass bottles at <5°C until analysis.

Sediment samples (minimum 50 g) were collected from the lake bottom using a grab sampler at points along the same transects as the water samples. These were decanted, placed in jars topped with tinfoil wrap and kept at <5°C until analysis. Sediment samples were screened in the laboratory for organic (invertebrate) material, but the quantities obtained were insufficient for confident analysis of brodifacoum concentration in actual invertebrate tissue (Table 1). Long-finned eels (n = 5, Table 1) captured by netting were euthanazed, bagged whole, chilled and sent for necropsy. The eels weighed 450–2,010 g each and were apparently healthy with full gastrointestinal tracts and no gross pathology observed. Livers were removed for brodifacoum analysis.

Two pied shags found dead in the lake on the second sampling visit were stored chilled and sent for necropsy. Both were adults (2,162 g and 2,160 g, respectively) but sex was not determined. In one bird death was most likely from severe impaction of the lower intestine by relatively large (up to 10 cm long, 4 cm wide) pieces of ingested wood. There was no obvious internal hemorrhage and all organs appeared normal. The other bird had blood visible around the mouth and beak that had leaked from free blood present in the chest cavity and pericardium. The site of the hemorrhage was at the top of heart, which was full of clotted blood. Other organs appeared healthy, with digesta present in the lower intestine. Liver tissue from both birds were analysed for brodifacoum concentration.

Table 1 Environmental sample types, numbers and dates collected from Lake Kirirua and results of testing for brodifacoum concentration

Sample type	Sampling date (2010)	Samples tested (n)	Brodifacoum concentration (ppm)
Lake water	26 June	17	<MDL
	08 July	10	<MDL
Lake sediment	08 July	7	<MDL
	30 July	9	<MDL
Lake invertebrates[a]	08 July	6	<MDL
Fish (*Anguilla diefenbachii*)			
Liver	30 July	5	<MDL
Bird (*Phalacrocorax varius*)			
Liver	08 July	2	<MDL

[a] Screened samples from lake-bottom sediment; inadequate quantities of invertebrate tissue obtained

All samples were analysed by the Landcare Research toxicology laboratory, New Zealand. Chopped samples of liver (2 g) or invertebrate (0.5 g) tissue were mixed with 15 mL of chloroform/acetone/ammonia, homogenized for 1 min at 135,000 rpm then centrifuged at 4,300 RCF (G) for 5 min. Supernatant was decanted and the extraction repeated twice more with 10 mL portions. Combined extracts were evaporated and taken up in chloroform/hexane for SPE clean-up on an aminopropyl column. The analyte was eluted from the column using TBAP (0.5 and 0.005 M, respectively) which was evaporated off and the sample taken up in mobile phase. For water samples, a C-18 solid-phase disk procedure was used to concentrate brodifacoum from 500 mL of sample and elute it with aliquots of acetone. The solvent was evaporated and the residue reconstituted with 1.0 mL of methanol/acetic acid/water mobile phase. Sediment samples were extracted with methanol. Brodifacoum concentrations were determined in all sample extracts by high performance liquid chromatography with fluorescence detected as described by Primus et al. (2005), using a C-18 column with a reversed-phase mobile phase and post-column pH switching technique to exploit the natural fluorescence of this compound. Difenacoum was used for internal quality control samples. Method detection limits (MDL) were 0.02 ppb for water, 50 ppb for sediment and invertebrate tissue, 5 ppb for eel

liver, and.1 ppb for shag liver. Liver and invertebrate tissue was analysed using validated methods, with respective uncertainties of ±6% and ±22%. Method recoveries calculated from concurrent analyses of brodifacoum-spiked samples (0.1 ppb in water, 0.025 μg in liver tissue, 0.05 μg in sediment) were 94%, >110% and >111%, respectively.

Results and Discussion

Results indicate that brodifacoum from spilled baits did not produce detectable concentrations in water during the 2 weeks following the spill. This result is consistent with other fresh water monitoring following aerial application (rather than a spill) of similar brodifacoum cereal baits (Fisher et al. 2011). Brodifacoum is at best sparingly soluble in water, and solubility reduces with water pH (British Crop Protection Council 2000). However, brodifacoum does bind strongly to organic matter (World Health Organisation 1995). Thus for cereal pellet baits entering a large body of fresh water, only a limited amount of the brodifacoum would enter solution, being more likely to remain bound to bait particles or to other organic particles present in the water or sediment.

The apparent absence of brodifacoum in lake sediment was probably because a relatively small estimated quantity (14 g) of brodifacoum entered a large lake, so that detectable concentrations were not present in sediment sampled at about 1 week and 1 month later. Given how the spill occurred, it was not possible to target sediment sampling to specific parts of the lake where bait was known to be present on the lake bed.

It was difficult to distinguish and separate samples of benthic invertebrate tissue from sediment to produce an adequate quantity for analysis. Thus results for 'invertebrates' represent organic sediment components that include small invertebrates. The lack of residues in five eels suggests that they were not exposed to brodifacoum as a result of the spill. The extensive internal hemorrhage in one shag may have had a number of causes, including anticoagulant poisoning. However, the <MDL result in liver tissue from this bird effectively ruled out recent exposure to brodifacoum and poisoning as a contributor to mortality. This result highlights the importance of conducting both necropsy and liver residue testing for post-mortem determinations of anticoagulant poisoning.

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