Assessing occupational exposure to sea lamprey pesticides

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Background: Sea lampreys are parasitic fish found in lakes of the United States and Canada. Sea lamprey is controlled through manual application of the pesticides 3-trifluoromethyl-4-nitrophenol (TFM) and BayluscideTM into streams and tributaries. 3-Trifluoromethyl-4-nitrophenol may cause irritation and central nervous system depression and Bayluscide may cause irritation, dermatitis, blisters, cracking, edema, and allergic skin reactions.

Objectives: To assess occupational exposures to sea lamprey pesticides.

Methods: We developed a wipe method for evaluating surface and skin contamination with these pesticides. This method was field tested at a biological field station and at a pesticide river application. We also evaluated exposures using control banding tools.

Results: We verified TFM surface contamination at the biological station. At the river application, we found surfaces and worker's skin contaminated with pesticides.

Conclusion: We recommended minimizing exposures by implementing engineering controls and improved use of personal protective equipment.

Keywords: Sea lampreys, Pesticides, TFM, Bayluscide, Wipe sampling, River application, Dermal exposure, Biological station, Lampricides

Introduction

Sea lampreys (*Petromyzon marinus*) are parasitic fish in lakes of the United States and Canada including the Great Lakes, the Finger Lakes, and Lake Champlain. They are considered an invasive species, decimating indigenous fish populations such as the lake trout, lake whitefish, chub, and lake herring. Sea lampreys are controlled primarily through manual application of pesticides into streams and tributaries to kill the larvae. The two commonly used pesticides are 3-trifluoromethyl-4-nitrophenol (TFM) and BayluscideTM. 3-Trifluoromethyl-4-nitrophenol is the primary pesticide. However, Bayluscide is used with TFM when TFM alone poses too much risk to nontarget organisms or is cost prohibitive (EPA 1999). An estimated 56 000 kg of TFM (CAS Registry Number: 88-30-2) and 1000 kg of Bayluscide (CAS Registry Number: 50-65-7) were applied in the United States (US) in 2012.¹ In a typical year, 30–40 US tributaries are treated with these pesticides.² Formulation types include TFM liquid concentrate (38%), TFM bar (solid), Bayluscide 70% wettable powder, Bayluscide 20% emulsifiable concentrate, and Bayluscide granular (3.2 and 5%).^{2,3} According to the U.S. Environmental Protection

Agency, required label (EPA 1999) liquid TFM is dangerous and poisonous while the bar form is dangerous. Bayluscide emulsifiable concentrate is labeled dangerous and should be handled with caution.³

Although standard operating procedures and protective measures are in place for the use of these pesticides,³ comprehensive exposure data have not been collected to assess applicators' potential health risks.² Skin contact appears to be the primary route of exposure to pesticides⁴; therefore, the objectives of our evaluation were to (1) develop an analytical method to assess contamination on work surfaces and skin and (2) field test this method at two locations where workers were potentially exposed to these pesticides to provide control recommendations to the worksites. As a secondary objective, we used control banding tools to evaluate two tasks at the river application to determine if similar controls to those determined by sampling are recommended.

Pesticides used to control sea lampreys

3-Trifluoromethyl-4-nitrophenol

3-Trifluoromethyl-4-nitrophenol is the primary chemical used to control sea lamprey larvae. Formulation types include TFM liquid concentrate and TFM bar (solid). No human health effects have been associated with handling this pesticide. Animal toxicological studies have demonstrated that ingestion of TFM

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may result in irritation of mucous membranes and may be fatal.³ Animal studies also show that skin contact with TFM may cause severe irritation but not skin sensitization. 3-Trifluoromethyl-4-nitrophenol ingestion may cause central nervous system depression, nausea, vomiting, dizziness, and drowsiness.³ 3-Trifluoromethyl-4-nitrophenol is not considered a carcinogen, and no significant reproductive effects were observed in animal studies. There are no occupational exposure limits for TFM.

Bayluscide

Bayluscide is available as a wettable powder, granule mixture, or concentrated liquid consisting primarily of niclosamide ethanolamine salt. Animal studies show that inhalation may cause upper respiratory tract irritation, coughing, and nasal discharge.³ These studies also show that skin contact causes mild irritation. Ingestion may cause adverse effects to the gastrointestinal and respiratory tracts and a hunched posture in some animal species.³ However, ingestion of niclosamide in animals is used for treating tapeworm.⁴ Animal studies show that skin contact with the concentrated liquid causes moderate to severe irritation, dermatitis, blisters, cracking, edema, allergic skin reactions (i.e. skin sensitization), and severe eye irritation. There has been one account of human skin sensitization on a sprayman.⁵ Niclosamide has been used for human cestode infections and human health ill effects or adverse drug reactions include gastrointestinal disturbances and anaphylactoid reactions.⁶ However, Pearson and Hewlett⁷ reported that skin rash on human beings ingesting niclosamide occurred rarely. Niclosamide ethanolamine salt is not considered a carcinogen, and no significant reproductive effects were observed in animal studies. There is no documentation to our knowledge in regard to long-term human toxicology studies or the interaction of both pesticides with each other and other additives. There are no occupational exposure limits for niclosamine or Bayluscide.

River application

Effective pesticide application usually requires maintaining an optimal water concentration for 10–12 continuous hours. The three types of river applications are primary, maintenance, and supplemental. The application process may last up to 10 days. A primary application occurs at the most upstream point of the waterway so the pesticides flow downstream; maintenance applications are performed downstream to maintain effective pesticide concentrations; and supplemental applications are made to still backwater areas and in low-discharge rivers to kill sea lamprey larvae and to prevent their escape into larger rivers.³ 3-Trifluoromethyl-4-nitrophenol liquid and Bayluscide wettable powder and emulsifiable concentrate are

used in primary and maintenance applications. 3-Trifluoromethyl-4-nitrophenol liquid, TFM bar, and granular Bayluscide are used in supplemental applications. Although procedures and equipment differ with each application and pesticide formulation,³ all require supervision and assistance of biological field technicians who prepare equipment, transport, mix, and apply pesticides into the river. Technicians also analyze river water samples in portable laboratories to measure pesticide concentrations throughout a treatment period. Because pesticide concentrations in water can vary, continuous monitoring is necessary.³ In the US, there are 38 employees working in two biological stations that are potentially exposed to the lampriocides. Most of the employees work in 10-day periods throughout the season (April–October).

Control banding

Control banding is a technique used to guide the assessment and management of workplace risks when occupational exposure limits are not available. Control banding helps employers select a control measure (for example dilution ventilation, engineering controls, containment, etc.) on the basis of a range or “band” of hazards (such as skin/eye irritant, very toxic, and carcinogenic) and exposures (small, medium, large). Although control banding has yet to be fully tested, its use is designed to offer ways to assess risks and choose relevant control measures for reducing occupational exposures. Controls recommended by control banding methods may still need to be reviewed by a health and safety professional to ensure that the control strategy and implementation are appropriate. Additionally, using control banding for the application of pesticides that are extremely toxic, have multiple exposure routes, or are aerosolized and sprayed over a large area may not be appropriate. Likewise, using control banding for tasks that involve multiple chemicals, chemicals that may have more hazardous health effects when mixed, and chemicals with insufficient toxicity data could result in an incorrect estimation of exposure potential. We believed that control banding methods were appropriate for TFM and Bayluscide applications because of (1) the limited application area, (2) the limited number of pesticides or other chemicals used, and (3) pesticides that do not appear to be highly toxic for the routes of exposure encountered in this setting. The National Institute for Occupational Health and Safety (NIOSH) Current Intelligence Bulletin: Qualitative Risk Characterization and Management of Occupational Hazards: Control Banding, a literature review and critical analysis provides a detailed review of the control banding methodology and enumerates strengths and weaknesses of the method and control banding tools.⁸

Figure 1 Yellow stain in a wall suspected of 3-trifluoromethyl-4-nitrophenol (TFM) contamination leaching from the ground.

Materials and Methods

Sampling locations

Biological station

The NIOSH Health Hazard Evaluation (HHE) Program received a request from a manager of a biological station concerning potential employee exposure from spills of sea lamprey pesticide that occurred at the station in the 1960s and 1970s.⁹ The office employees believed that visible stains on the carpet, floors, and walls of the biological station were from TFM leaching from the ground. Figure 1 shows the yellow stain on a wall, presumably from TFM contamination. We collected wipe samples from surfaces that had visible yellow stains, and bulk carpet samples to determine if the yellow staining was TFM. We also took wipe and carpet samples from areas that were not visibly stained for comparison and to evaluate if contamination may have been spread by foot traffic from current TFM applications.

River application

The NIOSH HHE Program received a request from a government agency health and safety manager concerning potential exposures when employees manually applied pesticides into rivers to control sea lamprey larvae.¹⁰ We visited the river application sites twice to learn about health and safety concerns, observe work processes and practices, and assess exposures to pesticides. The primary objective of the sampling at this worksite was to assess skin exposure to TFM and Bayluscide. We observed employees mixing and applying TFM liquid and Bayluscide wettable powder at a primary application and TFM liquid, TFM bars, and Bayluscide granular at supplemental applications. Figure 2 shows the mixing of Bayluscide wettable powder. We collected wipe samples for pesticides from work surfaces, employees' work clothing, and exposed skin. We also collected wipe samples from employees' hands to see if their

Figure 2 Manual pouring of the Bayluscide wettable powder pesticide into two large vats before it is pumped into a river.

gloves protected the skin from pesticides. Results from the evaluation at the river application, including confidential medical interviews with employees, were published in the NIOSH HHE report.¹⁰

Sampling methods

Wipe and bulk sampling procedure

We used 4 × 4 in polyester AlphaWipes® (Texwipe, ITW Company, Kernersville, NC USA) prewetted with 4 milliliters (ml) of 50% isopropyl alcohol and 50% water and stored individually in 9-ounce glass jars with polytetrafluoroethylene-lined screw caps (see Fig. 3). Wearing clean gloves, we opened the wipe container and removed the wetted wipe. We used a 10 × 10 centimeter (cm) disposable cardboard template when possible to outline the surface that we sampled. For uneven or irregular surfaces, we estimated the sample area. Using one side of the wipe, we wiped the surface using repeated horizontal motions. We folded the wipe in half and wiped the same surface area, but this time wiping at a right angle (vertically) to the first wiping motion.

Figure 3 Wipe sampling on skin of employee after applying pesticides.

For hands, we asked the employees to wipe their hands for approximately 30 seconds as if they were cleaning their hands. We also collected a 1 × 1 cm bulk carpet sample where carpeting of the biological station was visibly stained yellow and another from an area without visible staining. In both instances, the carpet was glued directly to the unsealed concrete floor. All bulk and wipe samples were placed into labeled 20 ml amber glass vials with polytetrafluoroethylene-lined screw cap closures. Samples were kept at approximately 50°F (10°C) during transport and in the laboratory.

Sample preparation

Samples were extracted by adding methanol extraction solvent (10 ml for wipe samples and 120 ml for bulk samples) to each jar with subsequent shaking for 60 minutes. After shaking, approximately 3 ml of extract was filtered through a 13- mm polytetrafluoroethylene syringe filter and transferred to a 4-ml amber glass vial. An aliquot of the filtered extract was transferred to an autosampler vial and analyzed by high-performance liquid chromatography.

Sample analysis

A single chromatographic method was developed to provide separation of TFM and niclosamide (active ingredient of Bayluscide). The sample analysis was performed using a high-performance liquid chromatograph consisting of a Waters 2690 Alliance separations module and a Waters 996 photodiode array detector. 3-Trifluoromethyl-4-nitrophenol and niclosamide were separated using a 10 microliter (μl) injection volume on a Zorbax Eclipse XDB-C18 column (3.0 × 250 mm 5 μm particle size) using a gradient mobile phase program at a flow rate of 0.5 ml/minute. The mobile phase gradient employed 0.1% phosphoric acid in deionized water (v/v) and methanol with initial conditions at 60% methanol for 7 minutes, a linear ramp to 90% methanol at 8 minutes, hold at 90% methanol to 15 minutes, then linear ramp to 60% methanol at 16 minutes followed by equilibration for 8 minutes. The total run time was 24 minutes. Calibration and quality control were performed using analytical standards prepared from neat reference materials of TFM (Sigma-Aldrich N27802-5G, Lot MKBD8547V, 99%) and niclosamide (ChemService PS-1207, Lot 459-96A, 99.5%). Stock and calibration solutions were prepared in methanol. The limits of detection (LODs) for wipes were 0.7 microgram (μg) for TFM and 0.3 μg for niclosamide. The limits of quantitation (LOQs) for wipes were 2.3 μg for TFM and 1.0 μg for niclosamide. The analytical range was up to 700 μg/wipe for both TFM and niclosamide. Sample extracts above the analytical range were diluted to a level within the range and analyzed.

Control banding tools applied to the river application

We selected three of the most commonly used control banding tools to evaluate inhalation and dermal exposure hazards associated with mixing Bayluscide wettable powder with water in a vat and pouring TFM liquid into a vat. We chose these tasks because they involved employees handling the largest amount of pesticides.

The first control banding tool we used, Control of Substances Hazardous to Health (COSHH) Essentials, was developed by the Health and Safety Executive.¹¹ To evaluate the health hazard of the material we selected an appropriate risk phrase (R-phrase). The R-phrase describes the special risks associated with chemical substances. R-phrases are defined by the European Union and are found internationally in safety data sheets. With the implementation of the Globally Harmonized System of Classification and Labeling of Chemicals, hazard statements and their corresponding alphanumeric codes (H-codes) will eventually replace R-phrases; however, at this time, the control banding toolkits still use R-phrases. On the basis of the R-phrase, the control banding tool places the material into one of the five groups labeled A–E, with A being the least hazardous group and E the most hazardous group. To determine the exposure potential of the task, the evaluator identifies the dustiness or volatility of the chemical, choosing from low, medium, or high levels of dustiness or volatility. The evaluator also notes the quantity used or generated (small, medium, or large quantity). The COSHH Essentials tool then combines the results from these two steps and assigns the task to one of the four control strategies.

The second control banding method we used was the International Chemical Control Toolkit from the International Labor Organization.¹² Using this method, the evaluator assigns the chemical of concern to a hazard respiratory group on the scale from A (safest) to E (most dangerous). Like the COSHH Essentials, this method uses the dustiness or volatility of the chemical, the quantity used, and R-phrases to make this selection.

The third control banding method we used was the chemical management guide for dermal hazards developed by the German agency Deutsche Gesellschaft für Internationale Zusammenarbeit (GIZ).¹³ This method uses R-phrases to classify chemicals that cause damage through skin contact or absorption into five risk groups (classified A–E). Depending on the amount, the hazard category is basic (lowest hazard), advanced (medium hazard), or special (highest hazard).

We used the COSHH Essentials online toolkit and the International Chemical Control Toolkit to evaluate the respiratory hazards associated with mixing Bayluscide wettable powder with river water

and pouring TFM liquid into a vat. We used the GIZ chemical management guide dermal toolkit to evaluate the recommended level of protection for both tasks. Neither the COSHH Essentials nor the International Chemical Control Toolkit has fully developed a dermal exposure method.

Results

Biological station

During our evaluation, we learned that in the 1990s an environmental consulting firm was hired by the managers at the biological station. This firm tested the soil and groundwater for residual TFM contamination from spills. 3-Trifluoromethyl-4-nitrophenol was detected in soil and groundwater samples, but no further action was recommended. In 1998, approximately 2750 square feet of pesticide-contaminated concrete flooring was removed and replaced with new concrete that was subsequently sealed and painted. The concrete floor beneath the maintenance office, map room, and offices was not replaced because no TFM leaks had been suspected in these areas. However, no TFM sampling was conducted to confirm this. Since 1998, areas of the floor adjacent to where the concrete was removed and replaced had turned yellow (presumably from TFM) following contact with water, and in February 2012, yellow stains were noticed in the office carpet. The bulk sample with the visible yellow stain had a higher loading of TFM (6000 µg/sample) compared to the carpet sample that was not visibly stained (50 µg/sample).

A description of visible stains and the corresponding TFM concentrations from wipe samples collected at the biological station are presented in Table 1. For surfaces not visibly stained, TFM was either not detected (<0.7 µg/sample) or present in lower amounts (range 2.2–17 µg/sample) compared to TFM results from visibly stained surfaces (210–3700 µg/sample). Only one wipe sample that was visibly stained (1.5 µg/sample) was below 200 µg/sample.

River application

We observed that employees applying TFM wore short or long sleeve shirts, long pants, boots, waders, water resistant aprons, and 20-mil thick gloves made of neoprene and natural rubber latex. Coveralls and rubber aprons were used by employees during the primary application, and most of the times used during low flow rate applications. Most employees wore safety glasses, goggles, or a face shield when applying TFM liquid. No respiratory protection was required or used for the handling of TFM liquid in primary, maintenance, or supplemental applications.

We also observed employees applying Bayluscide wore long sleeve shirts, long pants, waders, and same gloves as those used for TFM or all natural rubber latex. In addition, employees wore safety glasses and half mask or full facepiece elastomeric respirator with organic vapor and N95 cartridges.

Results of the wipe sampling of work surfaces, clothing, and skin are in Tables 2–4. Some of the highest surface contamination levels were from surfaces with visible yellow stains during the primary

Table 1 Pesticide results from surface wipe samples at biological station

Wipe surface description	Visible yellow	TFM
	stain	µg/sample
Carpet from photocopy room*	Yes	(1.5) [†]
Wall in the workshop area*	Yes	310
Floor on the side of a drain on the workshop area*	Yes	520
Wall near small storage room in workshop area*	Yes	3700
Floor inside small storage room in workshop area*	Yes	390
Floor corner outside office near workshop area*	Yes	2600
Floor of pesticide storage area, back of warehouse*	Yes	210
Floor of pesticide storage area, front of warehouse*	Yes	2300
Carpet underneath furniture in office*	No	ND
Mat in conference room, front of the break room*	No	ND
Refrigerator handle in lunchroom	No	ND
Forklift steering wheel	No	5.3
TFM liquid container handle	No	4.5
Workshop floor (sealed old concrete)*	No	12
Employee 1 boot bottom surface*	No	(2.2)
Employee 2 boot bottom surface*	No	17
LOD		0.7
LOQ		2.3

TFM: 3-trifluoromethyl-4-nitrophenol; LOD: limit of detection; LOQ: limit of quantitation; ND: not detected, below the LOD.

*Samples were taken from a 10 cm × 10 cm area.

[†]Values between the LOD and LOQ are shown in parentheses. There is more uncertainty associated with these values than with levels above the LOQ.

Table 2 Wipe sampling on employees' clothing for pesticides at river application

Work location	Employee number	Sample location	Niclosamide ^a µg/sample	TFM µg/sample
Primary application of TFM liquid and Bayluscide wettable powder	2	Rubber apron	1.5	86
	2	Hard hat	2.6	3.6
	3	Gloves on surface	ND	37
	4	Back shirt	1.3	13
	5	Boot wader	ND	41
	6	Inside respirator ^b	5.2	ND
	6	Cuff of the shirt	260	ND
	8	Inside boots	4.8	ND
	12	Bottom of boots	93	340
	17	Apron front	4.0	20
	17	Inside of hard hat	29	3.8
	20	Inside of apron	ND	(1.1) ^c
Supplemental application of TFM liquid	5	Sole of shoe	ND	8.5
	13	Goggles ^b	ND	67
	13	Apron	ND	99
	13	Cuff of the shirt	ND	40
	14	Back of shirt	ND	ND
	15	Glasses ^b	ND	ND
	16	Inside hip boots	ND	(2.0)
	16	Shirt	ND	100
	22	Cap cloth	ND	ND
	22	Boot front top	ND	ND
Supplemental application of TFM bars and Bayluscide granular	23	Inside waders	ND	ND
	24	Inside waders	ND	ND
	25	Inside waders	(0.65)	(1.8)
LOD			0.3	0.7
LOQ			1.0	2.3

TFM: 3-trifluoromethyl-4-nitrophenol; LOD: limit of detection; LOQ: limit of quantitation; ND: not detected, below the LOD.

^aNiclosamide is the active ingredient of Bayluscide.

^bThe area of the wipe sample was approximately 100 cm² because many surfaces were irregular.

^cValues between the LOD and LOQ are shown in parentheses. There is more uncertainty associated with these values than with levels above the LOQ.

application. Most skin surfaces that we wiped were contaminated with pesticides.

Pesticide surface and skin contamination was not surprising given that some employees wore short sleeves and pesticides could splash onto their bare arms. Employees used gloves, aprons, and other personal protective equipment (PPE) inconsistently, and some did not clean their PPE before reusing it. Some employees washed their hands with pesticide-treated river water.

Control banding for two tasks at the river application

Summary inputs used (i.e. R-phrases and exposure potentials) and outputs obtained (i.e. control level) with the control banding tools are summarized in Table 5. The full description of the process used to apply control banding tools to two tasks at the river application process are available in the NIOSH HHE report.¹⁰ Using control banding methods, the recommended controls were similar to those based on sampling results (e.g. use enclosed equipment for handling pesticides (containment) and personal protective equipment).

Task one: mixing bayluscide wettable powder with water

The COSHH Essentials and the International Chemical Control Toolkit assigned a health hazard band of “C”

to this task, meaning that it involves handling a “more hazardous substance.” Both methods recommended control level 3, “Containment” (i.e., fully enclosing the process), and suggested substitution with less hazardous materials as the primary means to reduce the hazard. The International Chemical Control Toolkit also recommended diluting concentrated pesticides.¹⁴

Using the GIZ chemical management guide skin toolkit, Bayluscide wettable powder is classified a skin hazard group C, “more hazardous substances.” It recommended an advanced control approach involving elimination or substitution, applying administrative or engineering controls, and using PPE. If substituting less hazardous chemicals or engineering and administrative controls were not possible, PPE was recommended to protect potentially exposed skin.

Task two: pouring TFM liquid into a vat

COSHH Essentials and the International Chemical Control Toolkit assigned this task to a hazard group of C, “more hazardous substances,” and recommended a control approach of level 3, “Containment.”

The GIZ chemical management guide dermal toolkit assigned TFM liquid to skin hazard group C, based on its R-phrase of R-24 (toxic in contact with skin), and recommended an advanced control approach involving elimination or substitution, applying engineering or administrative controls, and using PPE. If substituting a less hazardous chemical or engineering and adminis-

Table 3 Wipe sampling on surfaces for pesticides at river application

Work location	Sample location	Niclosamide ^a µg/sample	TFM µg/sample
Primary application of TFM liquid and Bayluscide wettable powder	Lunch box #a	ND	ND
	Lunch box #b	ND	ND
	Insulated water container spout ^b	(0.89) ^c	ND
	Nozzle on titrator ^b	38	23
	Yellow stain on concrete floor before leaning	3.4	1700
	Concrete floor after cleaning	ND	62
	Truck #5, driver inside door handle ^b	1.4	(1.4)
	Trailer back door handle ^b	(0.33)	ND
	Kit/tool box with PPE stored	1.7	10
	Truck #5, river floor pedals	1.4	18
	Cooler handle ^b	(0.88)	ND
Parking lot central location	Truck #1, steering wheel	ND	(2.0)
	Trailer handle on door ^b	ND	ND
	Truck #2, driver seat	1.1	2.5
	Truck #2, steering wheel ^b	2.8	14
	Truck #2, driver outside door handle	(0.68)	(1.5)
	Truck #3, steering wheel ^b	(0.42)	3.4
	Truck #3, driver outside door handle	ND	ND
	Truck #4, passenger door handles	ND	ND
	Truck #4, passenger seats	0.9	2.9
Supplemental application of TFM liquid	Truck # 6 tailgate, where lab work was done	ND	ND
	Trailer handle door ^b	ND	ND
	Lab bench top mobile lab	ND	(1.4)
	Door handle mobile lab ^b	ND	ND
Supplemental application of TFM bars and Bayluscide granular	Lab keyboard	ND	ND
	Boat steering wheel ^b	ND	12
	Boat throttle ^b	ND	8.5
	Boat motor control	ND	6.3
	Boat bilge, end of shift	(0.59)	210
LOD		0.3	0.7
LOQ		1.0	2.3

TFM: 3-trifluoromethyl-4-nitrophenol; PPE: personal protective equipment; LOD: limit of detection; LOQ: limit of quantitation; ND: not detected, below the LOD.

^aNiclosamide is the active ingredient of Bayluscide.

^bThe area of the wipe sample was approximately 100 cm² because surfaces were irregular.

^cValues between the LOD and LOQ are shown in parentheses. There is more uncertainty associated with these values than with levels above the LOQ.

trative control was not possible, PPE was recommended to protect potentially exposed skin.

Discussion

Biological station

We found TFM on wipe samples of carpet, floors, and walls. Lower amounts, down to three orders of magnitude of TFM, were measured in carpet and floor wipe samples taken from locations that had no visible stains compared to visibly stained surfaces, suggesting that TFM contamination could be identified by the yellow color. From our workplace observations, it appeared that visible stains were only present in areas where concrete had not been renovated or sealed, suggesting that current TFM handling practices were not contributing to ongoing surface contamination in the offices and workshop at the biological station. We do not know if the stains presented a health hazard to employees because of the lack of human toxicological data for TFM. However, as a preventative measure, minimizing contact with visibly stained surfaces would avoid skin exposures. We do not anticipate that TFM contamination on these surfaces would become airborne and pose a risk for inhalation.

The biological station had no written procedures for decontaminating field employees' clothing and PPE after they handled pesticides and before they entered the workshop and offices. However, the amount of TFM (<17 µg/sample) on wipe samples collected from the surfaces of two pairs of work boots that employees were wearing inside the offices after being in the field suggests that employees are not tracking TFM from the field or storage areas to the offices.

The amount of TFM measured on wipe samples taken from carpeted surfaces that were adjacent to visible stains was much less than the amount measured in the stained area of the carpet. This was unexpected and suggests that even if a carpet had visible stains (indicative of TFM contamination), the TFM on carpet may not be readily transferred to the surrounding carpet. However, these results should be interpreted with caution because no occupational guidelines for acceptable surface contamination of TFM have been established.

We recommended the government agency to remove the stained carpet and adhesive using a method that will not void the warranty for the replacement carpet or other floor coverings. The CRI

Table 4 Dermal wipe sampling for pesticides at river application

Worksite	Employee number	Sample location	Niclosamide ^a μg/sample ^b	TFM μg/sample ^b
Primary application of TFM liquid and Bayluscide wettable powder	1	Hands	1.2	3.9
	1	Hands, after washing	1.6	8.2
	2	Neck, yellow stained skin	ND	79
	3	Forearm	(0.88) ^c	(1.2)
	6	Hands, after washing	270	11
	7	Hands, beginning of shift	1.7	ND
	9	Hands, beginning of shift	ND	ND
	9	Hands, after washing	2.3	(1.4)
	10	Hands, before cotton liners	2.5	ND
	10	Hands, after cotton liners	1.7	ND
	11	Hands, before cotton liners	6	8
	11	Hands, after cotton liners	1.4	(0.81)
	12	Hands, after cotton liners	7.4	ND
	13	Hands	ND	110
	14	Hands	ND	9.0
	15	Neck	ND	ND
	16	Hands	ND	85
Supplemental application of TFM liquid	16	Hands, after washing	2.4	6.2
	16	Forearm, after washing	1.1	11
	17	Hands, after washing	6.4	12
	17	Neck, after washing	ND	ND
	19	Hands	150	58
	20	Hands, after washing	3.4	8.2
	21	Back of the hand	ND	ND
	21	Forearm	ND	ND
	22	Hands	ND	6.8
	23	Hands	ND	85
Supplemental application of TFM bars and Bayluscide granular	24	Hands	ND	78
	25	Forearm	ND	(1.4)
LOD			0.3	0.7
LOQ			1.0	2.3

TFM: 3-trifluoromethyl-4-nitrophenol; LOD: limit of detection; LOQ: limit of quantitation; ND: not detected, below the LOD.

^aNiclosamide is the active ingredient of Bayluscide.

^bSurface area for most skin sampled was approximate 100 cm² surface area except for hands. Hands were wiped for approximately 30 seconds.

^cValues between the LOD and LOQ are shown in parentheses. There is more uncertainty associated with these values than with levels above the LOQ.

Table 5 Control banding summary inputs and outputs*

Inputs		Outputs	
R-phrases	Exposure potential	Respiratory toolkits control level	Skin toolkit control level
Task one: Mixing Bayluscide wettable powder with water			
R-20/21/22: harmful by inhalation, in contact with skin, and by ingestion	Very dusty (fine light powder)	ILO ICCT: Level 3, containment	GIZ: Advanced control approach
R-22: harmful if swallowed			
R-34: causes burns	Medium quantity		
R-36: irritating to the eyes			
R-36/38: irritating to eyes and skin	Short task duration	COSHH Essentials: Level 3, containment	
R-50/53: very toxic to aquatic organisms			
Task two: Pouring TFM liquid into a vat			
R-10: flammable	Low volatility (solid in a liquid)	ILO ICCT: Level 3, containment	GIZ: Advanced control approach
R-22: harmful if swallowed	Large quantity		
R-24: toxic in contact with skin			
R-38: irritating to skin		COSHH Essentials: Level 3, containment	
R-41: risk of serious damage to eyes	Short task duration		
R-50/53: very toxic to aquatic organisms			

R-phrase: risk phrase; TFM: 3-trifluoromethyl-4-nitrophenol; ILO ICCT: International Labor Organization International Chemical Control Toolkit; COSHH: Control of Substances Hazardous to Health; GIZ: Deutsche Gesellschaft für Internationale Zusammenarbeit.

*Detailed description of inputs and outputs are included in the National Institute for Occupational Health and Safety (NIOSH) Health Hazard Evaluation (HHE) report.⁹

Carpet Installation Standard does not recommend the use of liquid adhesive removers on a concrete slab that will receive a new floor covering installed with adhesive.¹⁵ We also recommended cleaning and sealing concrete in the biological station that had not been previously remediated or sealed.

River application

We found pesticides on work surfaces and employees' skin and clothing. Although there are no occupational exposure limits for surface contamination with these pesticides, our results highlight the need to improve practices to minimize skin exposure. Hand contamination may indicate that employees were touching contaminated surfaces with bare hands, reusing contaminated gloves, or not using protective gloves when necessary. Because TFM and Bayluscide have low vapor pressure,^{16,17} inhalation exposures are unlikely, unless the pesticides are aerosolized (e.g. spills, splashes).

Respirators were required during the primary application when applying Bayluscide wettable powder. Employees wore full facepiece or half mask elastomeric respirators equipped with combination volatile organic compound and N95 filter cartridges. There is no information on the efficacy of these respirator cartridges against Bayluscide, and the pesticide labels do not recommend the use of respirators. Prior air sampling found that exposures to crystalline and amorphous silica in the Bayluscide wettable powder were well below occupational exposure limits. Considering that application of Bayluscide wettable powder occurs during the summer months on potentially very hot days, wearing respirators places additional heat stress on employees. The level of respiratory protection could be reduced on the basis of the agency's review of protective standard operating procedures, good work practices, and improved engineering controls.

We saw employees transferring, handling, and mixing TFM liquid and Bayluscide wettable powder in open containers. Spills and dust from mixing could be reduced if enclosed equipment were provided. For example, the open mixing vats used in the primary application of TFM liquid could be enclosed and TFM liquid transferred by tube from prepackaged containers to the vats. The same could be done for the transfer and mixing of Bayluscide wettable powder in primary and maintenance applications.

We recommended the agency to use the sampling methodology described here to assess surface contamination as interventions in the workplace are implemented. Similar wipe sampling methods have been used successfully for assessing pesticide exposures.^{18,19} Similar to conclusions found in the study by Zalk *et al.*²⁰ and Hashimoto *et al.*,²¹ we determined that

control banding could be used to assess interventions or even other tasks in the future, especially since TFM and Bayluscide do not have occupational exposure limits. The examples using control banding showed how to successfully use control banding for tasks involving TFM and Bayluscide.

Conclusion

At the biological station, we found TFM on carpet, floors, and walls with visible yellow stains. With one exception, we did not find TFM on surfaces that were not visibly stained. All of the visible yellow stains in the workshop and offices were likely related to the spills that occurred in the past (1960s and 1970s). Visibly stained surfaces were associated with concrete that had been neither remediated nor sealed. Current work practices were not contributing to ongoing surface contamination in the workshop and offices and no additional environmental monitoring was needed. At the biological station, we recommended changing contaminated flooring and sealing concrete and walls that were visually contaminated.

At the river application, we observed inconsistent use and inappropriate reuse of PPE and inconsistent hand washing methods. We detected pesticides on work surfaces, personal clothing, and skin of employees. We observed the transfer, handling, and mixing of pesticides in open containers. Sampling results and control banding tools suggested enclosing pesticide containers and consistent and correct use of personal protective equipment as primary means to control exposures.

The described wipe sampling and analysis methodology was able to identify contamination of sea lamprey pesticides, TFM and Bayluscide, in two workplaces. The wipe sampling method could be further used to assess work surfaces and skin contamination in the field to determine successful interventions to reduce dermal exposure to sea lamprey pesticides. We recommended the agency to use the sampling and analysis method described here or to use the control banding tools for future assessment of work hazards related to TFM and Bayluscide, specifically if there are any changes in application procedures.

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Disclaimer Statements

Contributors KK: chemical analysis method development, wrote report of lab results, and reviewed the manuscript. KM: medical and field assistance and contributed to writing reports and manuscript. CCB: industrial hygiene field assistant, control banding assessment, and contributed writing reports and manuscript. DMC: lead of the projects, industrial hygiene field sampling, and lead writer of reports and manuscript.

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Conflicts of interest None.

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References

- 1 Integrated management of sea lampreys in the Great Lakes 2012 – annual report to the Great Lakes Fishery Commission [document from internet]. Great Lakes Fishery Commission; 2013 [cited 2014 November]. Available from: http://www.glfc.org/sealamp/ANNUAL_REPORT_2012.pdf
- 2 Environmental Protection Agency (EPA). Reregistration eligibility decision (RED) 3-trifluoro-methyl-4-nitrophenol and niclosamide. Environmental Protection Agency. United States Prevention, Pesticides and Toxic Substances (7508C). Washington, DC: EPA 738-R-99-007; 1999.
- 3 U.S. Fish and Wildlife Service. Standard operating procedures for application of lampricides in the Great Lakes Fishery Commission integrated management of sea lamprey (*Petromyzon marinus*) control program. Marquette, MI: SLC 92-001.4; 2004 April 16.
- 4 Niclosamide [document from internet]. TOXNET Toxicology Data Network; 2014 [updated 2002 November; cited 2014 November]. Available from: <http://toxnet.nlm.nih.gov/cgi-bin/sis/search/a?dbs+hsdb:@term+@DOCNO+1572>
- 5 Hayes WJ, Laws ER Jr. Handbook of pesticide toxicology: volume 3. Classes of pesticides. New York, NY: Academic Press, Inc.; 1991. p. 1498.
- 6 Bagheri H, Simiand E, Montastruc JL, Magnaval JF. Adverse drug reactions to anthelmintics. *Ann Pharmacother*. 2004;38(3):383–8.
- 7 Pearson RD, Hewlett EL. Niclosamide therapy for tapeworm infections. *Ann Intern Med*. 1985;102(4):550–1.
- 8 National Institute for Occupational Safety and Health (NIOSH). Qualitative risk characterization and management of occupational hazards: control banding. Cincinnati, OH: U.S. Department of Health and Human Services, Centers for Disease Control and Prevention, National Institute for Occupational Safety and Health. DHHS (NIOSH) Publication No. 2009–152; 2009.
- 9 National Institute for Occupational Safety and Health (NIOSH). Health hazard evaluation report: sea lamprey control pesticide contamination at a biological station. Ceballos D, editor. Cincinnati, OH: U.S. Department of Health and Human Services, Centers for Disease Control and Prevention, National Institute for Occupational Safety and Health, NIOSH HETA No. 2012-0164-3174; 2013.
- 10 National Institute for Occupational Safety and Health (NIOSH). Health hazard evaluation report: evaluation of employee exposures during sea lamprey pesticide application. Ceballos D, Musolin K, Beaucham C, editors. Cincinnati, OH: U.S. Department of Health and Human Services, Centers for Disease Control and Prevention, National Institute for Occupational Safety and Health, NIOSH HHE No. 2011-0099-3211; 2014.
- 11 Control of Substances Hazardous to Health (COSHH). Essentials [document from internet]. Health and Safety Executive; 2014 [cited 2014 November]. Available from: <http://www.hse.gov.uk/coshh/essentials/index.htm>
- 12 The International Chemical Control Toolkit [document from internet]. The International Labor Organization; 2014 [updated 2006 June; cited 2014 November]. Available from: http://www.ilo.org/legacy/english/protection/safework/ctrl_banding/toolkit/icct/
- 13 GTZ Chemical Management. Guide for small and medium sized enterprises [document from internet]. The German agency Deutsche Gesellschaft für Internationale Zusammenarbeit (GTZ); 2007 [cited 2014 November]. Available from: <http://www2.gtz.de/dokumente/bib/07-0702.pdf>
- 14 ILO Toolkit Control. Sheet P100 pesticide control approach 2 protective equipment [document from internet]. International Labor Organization (ILO); 2014 [cited 2014 November]. Available from: http://www.ilo.org/legacy/english/protection/safework/ctrl_banding/toolkit/icct/sheets/tcs-p100.pdf
- 15 CRI carpet installation standard [document from internet]. The Carpet and Rug Institute; 2011 [cited 2014 November]. Available from: http://www.carpet-rug.org/documents/publications/CRI_Carpet_Installation_Standard_2011.pdf
- 16 Dawson V. Environmental fate and effects of the lampricide bayluscide: a review. *J Great Lakes Res*. 2003;29(1):475–92.
- 17 Hubert TD. Environmental fate and effects of the lampricide TFM: a review. *J Great Lakes Res*. 2003;29(1):456–74.
- 18 Geno PW, Camann DE, Harding HJ, Villalobos K, Lewis RG. Handwipe sampling and analysis procedure for the measurement of dermal contact with pesticides. *Arch Environ Contam Toxicol*. 1996;30(1):132–8.
- 19 A literature review of wipe sampling methods for chemical warfare agents and toxic industrial chemicals [document from internet]. Environmental Protection Agency (EPA); 2007 [cited November 2014]. Available from: <http://www.epa.gov/esd/cmb/pdf/epa-600-r-07-004.pdf>
- 20 Zalk DM, Kamerzell R, Paik S, Kapp J, Harrington D, Swuste P. Risk level based management system: a control banding model for occupational health and safety risk management in a highly regulated environment. *Ind Health*. 2010;48:18–28.
- 21 Hashimoto H, Goto T, Nakachi N, Suzuki H, Takebayashi T, Kajiki S, et al. Evaluation of the control banding method-comparison with measurement-based comprehensive risk assessment. *J Occup Health*. 2007;49:482–92.