Sea Lamprey Pesticide Contamination at a Biological Station

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Contents

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Highlights Page

The Health Hazard Evaluation Program received a request for a health hazard evaluation from the manager at a biological station in Michigan. The request concerned surface contamination from spills of sea lamprey pesticides that occurred at the biological station in the 1960s and 1970s.

What We Did

- We visited the biological station in August 2012.
- We took samples of carpet that we thought may have been contaminated with pesticide.
- We took wipe samples from surfaces to check for pesticide contamination.
- We measured temperature, relative humidity, carbon monoxide, and carbon dioxide in the offices.
- We checked the heating, ventilation, and air-conditioning system in the offices and laboratory.
- We talked to employees and managers about the pesticide contamination.

We evaluated a biological station because managers were concerned about spills of sea lamprey pesticide that occurred in the 1960s and 1970s. We saw yellow stains on carpet, concrete floors, and walls and found pesticide on carpet and wipe samples that we collected from these stained areas. We recommend removing the stained carpet from the offices and cleaning and sealing the concrete floor and walls that have visible yellow stains.

What We Found

- Some areas of the poured concrete floor in the biological station had been cleaned and sealed.
- We saw yellow stains on the concrete floor that had not been cleaned or sealed.
- We found pesticide on the carpet and wipe samples from areas that were visibly stained.
- The carpet in the offices had been installed over unsealed concrete.
- Room air flowed from the offices into the workshop. This helped keep potentially contaminated air from entering the offices.
- The exhaust fan in the laboratory solvent storage room was not always turned on. This allowed air to flow into the nearby laboratory.

What the Employer Can Do

- Remove carpet with stains you can see.
- Clean and seal the concrete slab floor before installing new flooring.
- Clean, seal, and repaint walls that have stains you can see.

What the Employer Can Do (continued)

- Run the exhaust fan in the laboratory solvent storage room all the time. This should reduce the amount of solvent vapors that enter the nearby areas.
- Stop sampling soil and concrete that may have been contaminated from past spills.
- Tell employees about plans to renovate the building.

What Employees Can Do

- Avoid touching stained surfaces.
- Do not go into offices while wearing clothes, shoes, or materials that may have pesticides on them.
- Wash your hands with soap and water after you handle pesticides.

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Abbreviations

µg	Microgram
cm	Centimeter
CO_2	Carbon dioxide
CO	Carbon monoxide
DMF	Dimethylformamide
HHE	Health hazard evaluation
HVAC	Heating, ventilation, and air-conditioning
IEQ	Indoor environmental quality
mL	Milliliter
NAICS	North American Industry Classification System
NIOSH	National Institute for Occupational Safety and Health
ppm	Parts per million
PTFE	Polytetrafluoroethylene
TFM	3-Trifluoromethyl-4-nitrophenol

Introduction

The Health Hazard Evaluation (HHE) Program received a request from the manager of a biological research station in Michigan concerning potential employee exposure from spills of sea lamprey pesticide at the biological station in the 1960s and 1970s. The active ingredient in the pesticide is 3-trifluoromethyl-4-nitrophenol (TFM) (chemical abstract service registration number 88-30-2), with dimethylformamide (DMF) as the carrier solvent (chemical abstract service registration number 68-12-2). Additional information on the toxicity of TFM is in Appendix A. The office employees at the biological station believed that visible stains on the carpet, floors, and walls of the biological station were from TFM leaching from the ground. On August 22, 2012, National Institute for Occupational Safety and Health (NIOSH) investigators evaluated the biological station.

During the evaluation NIOSH investigators met with managers and union and employee representatives to discuss the HHE request. The objectives of our evaluation were to determine if the visual contamination at the biological station was due to TFM and to evaluate whether current pesticide use and handling practices were contaminating work surfaces in the biological station. An interim letter with preliminary recommendations, dated September 6, 2012, was sent to the biological station manager and an employee representative.

Background

The biological station was a one-story building of approximately 19,000 square feet. The offices, conference room, lunchroom, laboratory, and records/library/computer room were heated and air-conditioned. The workshop, trailer bay work area, and pesticide storage area were naturally ventilated. The maintenance office and map room were small noncarpeted spaces adjacent to the workshop. The main function of the biological station was to store and distribute TFM pesticide, primarily as a liquid concentrate containing 38% TFM [EPA 1999; U.S. Fish and Wildlife Service 2004].

The TFM concentrate was dark brown or red with a phenolic odor. At the time of our evaluation TFM barrels were stored in the southwest area of the biological station. However, in the 1960s and 1970s when the pesticide leaks reportedly occurred, the TFM was stored in the northeast area of the building.

In the 1990s, an environmental consulting firm hired by the managers at the biological station tested the soil and groundwater for residual TFM contamination from spills. TFM was detected in soil and groundwater samples, but no further action was recommended. In 1998, approximately 2,750 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 removed and replaced because no TFM leaks had been suspected in these areas, but no sampling for TFM was conducted in the offices to confirm this.

Since 1998, areas of the floor adjacent to where the concrete had been removed and replaced had turned yellow (presumably from TFM) when it came in contact with water, and in February 2012 yellow stains were noticed in the office carpet. Two office employees requested relocation because of these stains.

Methods

Approximately 10–50 employees work outside the biological station conducting field activities. At the time of this evaluation about 12 employees were present during the work day.

During a walk-through survey of the biological station we looked for visual evidence of water damage, water incursion, mold, and other potential indoor environmental quality (IEQ) problems. Spot measurements were taken for temperature, relative humidity, carbon monoxide (CO), and carbon dioxide (CO_2) (employee comfort parameters) using a Velocicalc® Plus Indoor Air Quality Monitor, Model 9565-P (TSI Incorporated, Shoreview, Minnesota) equipped with an IEQ probe. We evaluated the heating, ventilation, and air-conditioning (HVAC) system that served the office and laboratory areas by using ventilation smoke tubes and the Velocicalc® differential pressure probe.

We collected a 1 centimeter (cm) × 1 cm bulk carpet sample where the carpet was visibly stained yellow. We collected another carpet sample from an area that was not visibly stained underneath a desk. In both instances the carpet was glued directly to the unsealed concrete floor.

We also collected wipe samples using Texwipe® Alpha Wipe, Polyester 4 inch × 4 inch, part number TX1004 (ITW Texwipe, Kernersville, North Carolina) prewetted with 4 milliliter (mL) of a 50% isopropyl alcohol/50% water solution. We used a 10 cm × 10 cm disposable cardboard template whenever possible. A new pair of nitrile gloves was used per wipe sample to avoid cross contamination. Using only one side of the wipe, the designated area of the surface was wiped using repeated horizontal motions first. Then, the same surface area was wiped again using another side of the wipe (after folding the wipe once in half), but wiping at a right angle to the first wiping motion. Finally, the same surface area was wiped for the third time using another side of the wipe (after folding the wipe again), but wiping at a 45-degree angle to the first wiping motion.

Wipe samples were collected from the carpet adjacent to where the carpet bulk samples were collected. We took these wipe samples to determine if any contamination may have been spread by foot traffic. Wipe samples from surfaces such as floors and walls that had visible yellow stains were also collected throughout the biological station. We took samples from surfaces that were not visibly stained for comparison.

All bulk and wipe samples were placed into labeled 20 mL amber glass vials with polytetrafluoroethylene (PTFE)-lined screw cap closures. Samples were kept at approximately 50°F (10°C) during transport and in the laboratory. In the laboratory, samples were analyzed for TFM following an in-house method (Appendix B).

We did not analyze for DMF because we believed it was unlikely to still be present after 40 years in the ground. DMF is completely miscible with water and most organic solvents, and it is susceptible to microbial and algal degradation in water [International Programme on Chemical Safety 2013; ScienceLab 2013].

Results

Because the temperatures were mild, the garage doors to the workshop, trailer bay, work, and storage areas remained open during the workday. As a result the indoor temperature, relative humidity, and CO_2 were similar to outdoors. The CO concentration in these areas averaged 0.23 parts per million (ppm) (range 0.1 ppm to 0.3 ppm). The highest CO concentration was measured near a propane-powered fork lift in the trailer bay and storage areas.

In the offices, conference room, laboratory, server room, break room, and hall areas the average temperature was 74°F, and average relative humidity was 55%. The CO_2 concentrations in these areas averaged 887 ppm (range 566 ppm to 1,124 ppm), compared to an outdoor CO_2 concentration of 450 ppm. The CO concentrations in these areas ranged from 0 ppm to 0.1 ppm. Most of the offices were occupied by one to two employees. The conference room had from three to seven people during our visit.

The biological station managers were unable to provide information about the HVAC system, including how much outdoor air was introduced to the occupied spaces, the type of air filters, when these filters were last changed, or when the HVAC system was last serviced. However, our measurements suggest that the HVAC system serving the offices makes these areas under positive pressure relative to the workshop areas. This means that air flowed from the offices into the workshop. This helped prevent air contaminants from the workshop areas from entering the offices.

The exhaust fan in the laboratory solvent storage room did not operate continuously. When this fan was off the solvent storage room was under positive pressure relative to the adjacent laboratory, meaning that air flowed from the solvent storage room into the laboratory. This is the opposite of the desired air flow pattern to keep potential air contaminants in the storage room from entering the laboratory. However, when the exhaust fan was operating, the solvent storage room was under the desired negative pressure relative to the laboratory.

We observed yellow stains on the floors and walls in the workshop area and the adjacent noncarpeted maintenance office. These stains coincided with reports of where past pesticide spills had occurred. In the pesticide storage area, we observed yellow stains that may have resulted from recent spills. In the offices, we noticed a yellow stain on carpet that was directly over concrete that had not been remediated or sealed.

A description of visible stains and the corresponding TFM concentrations from two bulk samples collected at the biological station are presented in Table 1. As expected, the bulk sample with the visible yellow stain had a higher loading of TFM (6,000 micrograms [µg]/sample) compared to the carpet sample that was not visibly stained (50 µg/sample).

Table 1. Pesticide results from bulk carpet samples

Description*	Visible yellow stain	TFM (µg/sample)
Carpet sample from photocopy room	Yes	6,000†
Carpet sample underneath furniture in office	No	50
LOD		2
LOQ		8.1

LOD = limit of detection

LOQ = limit of quantitation

*Samples were 1 cm x 1 cm in size.

†Analytical range was 2–6,000 µg/sample.

A description of visible stains and the corresponding TFM concentrations from wipe samples collected at the biological station are presented in Table 2. For surfaces that were not visibly stained the TFM was either not detected (< 0.7 µg/sample), or present in lower loadings (range 2.2 to 17 µg/sample) than TFM loadings from visibly stained surfaces that were sampled (210 to 3,700 µg/sample). Only one wipe sample that was visibly stained (1.5 µg/sample) was below 200 µg/sample.

Table 2. Pesticide results from surface wipe samples

Wipe surface description	Visible yellow stain	TFM (µg/sample)
Carpet from photocopy room*	Yes	1.5†
Wallin 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	3,700
Floor inside small storage room in workshop area*	Yes	390
Floor corner outside office near workshop area*	Yes	2,600
Floor of pesticide storage area, back of warehouse*	Yes	210
Floor of pesticide storage area, front of warehouse*	Yes	2,300
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 boot bottom surface*	No	2.2†
Other employee boot bottom surface*	No	17
LOD		0.7
LOQ		2.2

LOD = limit of detection

LOQ = limit of quantitation

ND = not detected (< 0.7 µg/sample)

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

†Estimated value between the LOD and LOQ

Discussion

Indoor Environmental Quality Comfort Indicators and Carbon Monoxide

Temperature and relative humidity values in the offices and laboratory areas were within the ASHRAE-recommended thermal comfort guidelines for the summer season [ANSI/ASHRAE 2010b]. By comparing indoor and outdoor CO_2 concentrations we determined that the indoor occupied spaces (offices and laboratory) were adequately ventilated according to ASHRAE guidelines [ANSI/ASHRAE 2010a]. The CO concentrations (0–0.3 ppm) were likely from vehicles in the adjacent parking lot or from a propane-powered fork lift used in the workshop.

Pesticide Surface Contamination

We found TFM on wipe samples of carpet, floors, and walls. Lower amounts 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 and/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 (Appendix A). 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 personal protective equipment 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 employee 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 and laboratory.

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 (Appendix B).

Conclusions

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 is needed.

Recommendations

On the basis of our findings, we recommend the actions listed below. We encourage the biological station to use a labor-management health and safety committee or working group to discuss our recommendations and develop an action plan. Those involved in the work can best set priorities and assess the feasibility of our recommendations for the specific situation at the biological station.

Our recommendations are based on an approach known as the hierarchy of controls. This approach groups actions by their likely effectiveness in reducing or removing hazards. In most cases, the preferred approach is to eliminate hazardous materials or processes and install engineering controls to reduce exposure or shield employees. Until such controls are in place, or if they are not effective or feasible, administrative measures and personal protective equipment may be needed.

Elimination and Substitution

Eliminating or substituting hazardous processes or materials reduces hazards and protects employees more effectively than other approaches. Prevention through design, considering elimination or substitution when designing or developing a project, reduces the need for additional controls in the future.

1. Remove the stained carpet and adhesive using a method that will not void the warranty for the replacement carpet or other floor covering. The CRI 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 [CRI 2013].
2. Clean and seal concrete in the biological station that had not been previously remediated or sealed.
3. Follow the carpet manufacturer's instructions if new carpet is installed. Instead of carpet you may wish to consider a floor covering that would be easier to clean. If carpet is used, information on interior products and materials that have low chemical emissions is available at http://www.greenguard.org.
4. After the concrete is sealed, clean and repaint walls that have visible yellow stains.
5. Ensure acceptable IEQ during building renovation, as many IEQ complaints occur in buildings undergoing renovation. The following NIOSH website describes the necessary steps: http://www.cdc.gov/niosh/topics/indoorenv/ConstructionIEQ.html.

Engineering Controls

Engineering controls reduce employees' exposures by removing the hazard from the process or by placing a barrier between the hazard and the employee. Engineering controls protect employees effectively without placing primary responsibility of implementation on the employee.

1. Adjust the exhaust fan in the solvent storage room to run continuously.
2. Check and replace (if necessary) the air filters in the HVAC system.
3. Consult a qualified ventilation engineer to evaluate the design and operation of the HVAC system, including determining how much outdoor air is being introduced into the occupied spaces [ANSI/ASHRAE 2010a].

Administrative Controls

The term administrative controls refers to employer-dictated work practices and policies to reduce or prevent hazardous exposures. Their effectiveness depends on employer commitment and employee acceptance. Regular monitoring and reinforcement are necessary to ensure that policies and procedures are followed consistently.

1. Do not conduct additional surface or soil sampling for TFM in the biological station.
2. Avoid touching surfaces that are visibly stained.
3. Avoid entering the office with pesticide-contaminated clothes, shoes, or objects.
4. Wash hands with water and soap after handling pesticides.
5. Tell employees about any renovation project. For example, explain the steps involved in removing and replacing the carpet in the office and what to expect when the office is reoccupied.
6. After renovation projects are completed, follow up with employees to ensure that remedial action have eliminated visible TFM contamination on carpet, floors, and walls.

Appendix A: 3-Trifluoromethyl-4-nitrophenol Background and Health Information

TFM is the primary chemical used to control sea lampreys. Sea lampreys (*Petromyzon marinus*) are parasitic fish in the Great Lakes, the Finger Lakes, and Lake Champlain [EPA 1999]. The number of sea lampreys is controlled primarily through selective pesticide (also known as lampricide, lampreycide, larvicide) applications into streams and tributaries, where they live in the larval stage.

The Environmental Protection Agency regulates the use of lampricides [EPA 1999]. Pesticide labels and detailed standard operating procedures are required by the Environmental Protection Agency [EPA 1999; U.S. Fish and Wildlife Service 2004]. Liquid TFM is labeled dangerous and poisonous [U.S. Fish and Wildlife Service 2004]. Although specific human health effects have not been associated with the handling of lampricides, limited animal toxicological data is reported in the material safety data sheets and technical sheets.

The precautions for TFM are based on animal toxicology [U.S. Fish and Wildlife Service 2004]. From animal studies we know that inhalation exposure to TFM may result in irritation of mucous membranes, skin or eye exposure may cause irritation, and ingestion of the product may be harmful or fatal if swallowed. TFM may cause central nervous system depression with nausea, vomiting, dizziness, and drowsiness. TFM is not considered a carcinogen, and no significant reproductive effects were observed in animal studies. There are no occupational exposure limits for TFM.

Appendix B: 3-Trifluoromethyl-4-nitrophenol Analysis Method

Bulk and Wipe Sample Preparation

The bulk samples were extracted by adding 120 mL extraction solvent (methanol) to each jar with subsequent shaking for 60 minutes. After shaking, approximately 3 mL of extract was filtered through a 13-mm PTFE 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.

Surfaces wipes were extracted by adding 10 mL of extraction solvent (methanol) to each jar, and then shaken for 60 minutes. After shaking, approximately 3 mL of extract was passed through a 13-mm PTFE syringe filter and then 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

The bulk and wipe samples were desorbed and analyzed by high performance liquid chromatography with a photodiode array detector. The analytical range was 2–6,000 µg/sample. The limit of detection for bulks was 2 µg/sample; for wipes it was 0.7 µg/sample. The limit of quantitation for bulks was 8.1 µg/sample, and for wipes the limit of quantitation was 2.2 µg/sample. TFM had a recovery of > 98% and a precision of > 97%. The sample analysis method parameters were as follows:

1. Instrument: Waters 2690 separations module
2. Detector: Waters 996 photodiode array detector
3. Column: Zorbax Eclipse XDB-C18, 3.0 x 250 millimeters, 5 micrometers
4. Column flow rate: 0.5 mL/minute
5. Column temperature: 86°F (30°C)
6. Injection volume: 10 microliters
7. Detection wavelength TFM: 294 nanometers
8. Run time: 24 minutes
9. Elution time TFM: 7.1 minutes

The following gradient was used for the mobile phase:

1. 7 minute – 40% mobile phase 1/60% mobile phase 2
2. 8 minute – 10% mobile phase 1/90% mobile phase 2
3. 15 minute – 10% mobile phase 1/90% mobile phase 2
4. 16 minute – 40% mobile phase 1/60% mobile phase 2

5. 24 minute – 40% mobile phase 1/60% mobile phase 2
6. Mobile phase 1 = deionized water with 0.1% phosphoric acid
7. Mobile phase 2 = 100% methanol

Calibration and quality controlled was performed using stock analytical standards prepared from a neat reference material of 99% TFM, Aldrich N27802-5G, Lot MKBD8547V (Aldrich, Sigma-Aldrich, St. Louis, Missouri). Stock solutions were prepared in extraction solvent.

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Availability of Report

Copies of this report have been sent to the employer, employees, and union at the biological station. The state and local health department and the Occupational Safety and Health Administration Regional Office have also received a copy. This report is not copyrighted and may be freely reproduced.

This report is available at http://www.cdc.gov/niosh/hhe/reports/pdfs/2012-0164-3174.pdf

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