

Fire Research Report

The Ecotoxicity of Fire-Water Runoff Part II: Analytical Results

ESR

August 2001

This report contains the analytical results of chemical testing of sampled runoff from the scenes of four different common types of structural or vehicular fires in New Zealand during 2000. The report aims to compare the results of the chemical analyses of runoff with published water quality criteria for the protection of aquatic life in order to assess the ecological hazard potential of these events, and to identify contaminants contributing the most to the estimated risks

The results from the monitoring of 4 structural fires and 1 vehicular fire in this study are consistent with the runoff concentrations from different types of fires reported in other countries. The runoff from the autoshop fire was the most hazardous to aquatic life. A fire at a fruit shop yielded runoff with metal concentrations comparable to that found in a large industrial plastics warehouse fire overseas, although the volumes of runoff for the fruit shop fire were almost certainly much smaller. The runoff from the house fire presented the lowest ecotoxic hazard.

Undiluted, the runoff from all five fires would be acutely lethal to aquatic life, if it is assumed that even a fraction of the contaminants are bioavailable. The experience of ecosystems impacted by similar fires overseas indicates that the metal concentrations dissipate from the surface water within several days and do not pose a chronic hazard. It does appear therefore, that in most cases, the threat of lasting ecological damage is small, provided that the receiving waterway is of sufficient size and flow rate to reduce the acute impacts. No fires at chemical storage or other heavy industrial sites were available for sampling in the time period, but it is highly likely that runoff from fires at such facilities would be much more of a toxic threat than those fires in this report, and could result in ecological catastrophe for the aquatic life in the receiving waterway.

Dominique Noiton, Ph.D, Jefferson Fowles, Ph.D. and Helen Davies, M.Sc.
New Zealand Fire Service Commission Research Report Number 18
ISBN Number 0-908920-61-X
© Copyright New Zealand Fire Service Commission

**The Ecotoxicity of Fire-Water Runoff
Part II: Analytical Results**

A Report to the New Zealand Fire Service

June 2001

Client Report FW0121

The Ecotoxicity of Fire-Water Runoff
Part II: Analytical Results

Dominique Noiton, Ph.D.
Science Programme Manager

Jeff Fowles, Ph.D.
Project leader

Helen Davies, M.Sc.
Peer reviewer

DISCLAIMER

This report or document ("the Report") is given by the Institute of Environmental Science and Research Limited ("ESR") solely for the benefit of the New Zealand Fire Service.

Neither ESR nor any of its employees makes any warranty, express or implied, or assumes any legal liability or responsibility for use of the Report or its contents by any other person or organisation.

Acknowledgements

The author wishes to thank Chris Napier, Bill Butzbach, and Tony Haggarty of the New Zealand Fire Service for contributing to the sampling from the fire scenes. Thanks also to Dr Harry VanEnkevort of Agriquality New Zealand for the analytical work, Paula Beever of the New Zealand Fire Service for management of this project, and Dr Hamish Reid (Victoria EPA) for the original concept.

TABLE OF CONTENTS

1. PURPOSE OF REPORT	1
2. INTRODUCTION.....	1
3. METHODS	1
3.1 Study Design.....	1
3.2 Runoff Sample Collection	2
Sampling instructions	2
3.3 Chemical Analysis.....	3
3.4 Ecotoxicological Hazard Ranking	3
4. RESULTS	4
4.1 Metals.....	4
4.2 Organics.....	4
4.3 Water quality criteria.....	7
4.4 Ecotoxic hazards	8
5. DISCUSSION	11
6. CONCLUSIONS.....	13
7. REFERENCES.....	14
APPENDIX A: QUESTIONNAIRE AND DATA SHEET.....	15

1. Purpose of Report

This report contains the analytical results of chemical testing of sampled runoff from the scenes of four different common types of structural or vehicular fires in New Zealand during 2000. The report aims to compare the results of the chemical analyses of runoff with published water quality criteria for the protection of aquatic life in order to assess the ecological hazard potential of these events, and to identify contaminants contributing the most to the estimated risks.

This is the second in a series of three reports characterising the ecological risks associated with chemicals in fire-water runoff. The final report will scope the development of a risk assessment/risk management framework that incorporates considerations of the impacts on surrounding ecosystems from activities at fire-scenes into the emergency planning by authorities for priority facilities.

2. Introduction

A previous report: *The Ecotoxic Effects of Fire-Water Runoff, Part 1: Review of the Literature*, reviewed published information on several high-profile fires that resulted in significant and lasting ecological damage in other countries. In the previous report, the ecological impacts of fires from different chemical storage or manufacturing plants were described, along with any analytical chemistry data from the contaminated waterways. Preventative measures that could have been implemented to avert some of the impact of the runoff from these fires were also discussed.

The chemical analyses in this report are compared with sampled runoff from some of the overseas episodes, and with acute and chronic freshwater quality criteria for the protection of ecosystems from the United States Environmental Protection Agency (USEPA) and the Canadian Environmental Quality Guidelines for remediation of contaminated sites.

The dilution factors that would be needed over the course of an acute fire runoff pollution episode are calculated, and the risk of acute and lasting effects under various scenarios is discussed.

3. Methods

3.1 Study Design

Representative samples of fire-water runoff were to be taken opportunistically by fire-fighting personnel from any of the following types of fires:

- House fire
- Small business fires
- Vehicular fire
- Industrial/warehouse fire

Ten sampling kits were sent out to the regional fire service in Auckland. It was hoped that as many of these kits could be used as possible. However, the experience of the firefighters indicated that the collection of the samples was not always straightforward, was time consuming, and it was sometimes difficult to collect enough runoff and to distinguish the runoff from the water leaking from around the pumps. The flow rate of water used to combat the fire provides an overestimate of the true volume involved in the runoff since much of the water applied to the fire would be expected to evaporate before being carried off site. This overestimate helps provide a measure of conservatism in the calculation of risk estimates and dilution volumes.

3.2 Runoff Sample Collection

At each fire, samples were mixed and placed into the following containers for analysis:

- For metals, an acid preserved 100 ml plastic bottle
- For cyanide, an alkali preserved 500 ml plastic bottle
- For conductivity and pH, 500 ml unpreserved plastic bottle
- For PAHs, a 1litre sodium thiosulphate preserved glass bottle.
- For Volatile and Semi-volatile organics, a clean 250 mL glass bottle.

Chlorinated dioxins were not included in the sampling scheme due to the high cost of sample analysis.

Sample containers were filled to near full for each container, although there were some containers in one fire (sports store) that had a small residual air space in the sample bottles, potentially lowering the volatile organic concentration. Samples were kept on ice in a chilly bin and sent in a sealed chilly bin to Agriquality New Zealand laboratories for analysis within 24 hours of collection.

Plastic scoops and funnels for sample collection were provided with each kit.

Sample collection instructions were sent out with each kit. The instructions were:

Sampling instructions

Goal: To obtain a representative sample of water and/or foam run-off from a fire scene during or shortly after the fire-fighting.

To collect run-off:

- Label each bottle before sampling as follows:
 - Location:
 - Date and Time:
 - Sample number:
 - Sampler's name:
- Wear latex gloves (provided)
- Use a clean plastic bucket or plastic scoop (provided)

- ❑ Try to keep the liquid well mixed by swirling or stirring before pouring into funnel (provided) into each of the 4 provided containers. Make sure each container is at least 2/3 full, but leave some air space (this advice was changed after the first sample to indicate that there should be no air space). Clean scoop/bucket and funnel after use before the next sampling.
- ❑ Place filled containers into the chilly bin with cold-packs or ice until shipped to the designated lab (overnight storage in the refrigerator is **ok** if necessary).

Sample kits included:

- ❑ 4 sample containers
- ❑ latex gloves
- ❑ self-labelled chilly bin
- ❑ cold packs
- ❑ plastic scoop
- ❑ plastic funnel
- ❑ data sheets
- ❑ sampling instructions
- ❑ tape for sealing the chilly bin for shipping
- ❑ courier tickets

In addition to the sample kits, a questionnaire was included to help collect information on the fire scene and amount of water or fire-fighting material used (questionnaire shown in Appendix 1).

3.3 Chemical Analysis

Runoff samples were analysed at Agriquality New Zealand, Wellington Science Centre, using Inductively Coupled Plasma Mass Spectroscopy (ICPMS), ICPMS with acid extraction, liquid extraction gas chromatography (GC), or purge and trap GC/MS.

3.4 Ecotoxicological Hazard Ranking

The analytical results for the runoff were compared with freshwater quality criteria for the protection of aquatic life, using the U.S. Environmental Protection Agency (USEPA) Critical Concentrations for chronic or acute (maximum) allowable levels (Table 3). The Canadian Environmental Quality Guidelines (EQG) for protection of freshwater aquatic life were also examined and compared with the results where no USEPA value was available. The Canadian values are based on remediation of contaminated sites, and so are more appropriate as chronic ambient criteria rather than those arising from acute transient conditions.

In general, the acute (maximal) concentrations (CMC) were used to rank the ecotoxicity from a runoff event, as it was assumed the contamination of the waterway would be transient. For some compounds, like cadmium and mercury, the biomagnification properties were such that chronic (CCC or EQG) were used in place of the acute standards. The acute standards are based on a 96-hour exposure scenario, and it is

anticipated that most fire-water runoff episodes would cease and contaminants would dissipate by this time. The Canadian and USEPA chronic (CCC) water standards provide conservative benchmarks for an acute pollution episode.

Impacts from thermal heating of the waterway are not included in the toxicity ranking scheme, but this is an additional aspect to consider for fire-water runoff.

4. Results

There were five different types of fires in which samples were collected and analysed. The four fires included: 1) a vehicle fire, 2) a fruit shop, 3) a sports store, 4) a domestic house fire, and 5) an auto shop fire. Runoff from a major chemical fire (i.e. at a chemical storage warehouse or manufacturing plant) was not available during the time period of this project. The results of the chemical analyses for each type of fire sampled are shown in Table 1.

4.1 Metals

As can be seen in Table 1, most of the analysed metals were detected in the 5 sampled fires. Zinc was generally found in the highest concentration, followed by boron, barium, and lead. Mercury was the one metal analysed for that was only found in one fire: the fruit shop fire.

4.2 Organics

Organic constituents in runoff were much more variable and dependent upon the structure and contents involved. Refrigerant chemicals (e.g. bromodichloromethane and chlorodibromomethane – both freons) were predictably found in the runoff from the fruit shop, where refrigeration units could be found, but not in the other three fires. Styrene was found in all four fire runoffs, although in a much higher concentration from the car fire. Similarly, the car fire had high levels of other plastic monomers, including some alkylbenzenes, acrylonitrile, alpha-methyl styrene, and methylmethacrylate. The car fire also had high levels of benzene, toluene, ethylbenzene, and xylene (BTEX), which are significant constituents of gasoline.

The PAH content was limited to naphthylene, acenaphthylene and phenanthrene, and these were found in the fruit shop, sports store, and auto shop fires. Most of the PAH's in the analytical screen were not detected in the runoff (Table 2). The concentrations of PAHs from the auto shop fire were the highest by more than an order of magnitude.

Bis(2-ethylhexyl)phthalate, a commonly used plasticiser was found above the detection limit only in the sports store and domestic house fire runoffs. These levels were slightly above the Canadian water quality criteria, and are probably not an acute hazard.

Table 1. Analytical results from runoff sampling at four fire scenes, and published water quality criteria for protection of aquatic life (U.S. EPA, www.epa.gov/ost/standards/wqcriteria.html), or Canadian Environmental Quality Guidelines for Water: Aquatic life (www.ccme.ca/pdfs/ceqg_rcqe/summary_table_e.pdf). New Zealand’s drinking water criteria for protection of human health are shown for comparison.

Analyte	Car fire	Fruit shop	Sports store	House	Auto shop	LOD	USEPA – acute CMC	USEPA – chronic CCC	Canadian EQG	Drinking water standards (NZ)
	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
<i>Metals</i>										
Cadmium	0.044	0.034	0.011	0.0012	0.008		0.0043	0.0022	0.000017	0.003
Lead	0.61	1.1	0.22	0.17	1.6		0.065	0.0025	0.001–0.007	0.01
Arsenic	0.039	0.11	0.025	0.051	0.36		0.34	0.15	0.005	0.01
Antimony	0.21	0.041	0.11	0.75	0.022					
Boron	1.2	4.5	0.23	1.1	1.2					
Chromium	0.026	0.044	0.01	0.042	0.12		0.016	0.011	0.0089 (III) 0.001 (VI)	0.05
Copper	1.2	0.23	0.13	0.12	2.2		0.013	0.009	0.002-0.004	2
Zinc	11	15	1	1.6	4.7		0.12	0.12	0.03	
Nickel	0.074	0.027	0.007	0.013	0.027		0.47	0.052	0.025 – 0.15	0.02
Manganese	1.4	0.53	0.086	0.18	0.20					
Mercury		0.005				0.002	0.0014	0.00077	0.0001	0.002
Cobalt	0.043	0.027	0.015	0.01	0.007					
Barium	2.2	1.2	0.62	0.82	0.63					
Tin	0.04	0.028	0.006	0.021	0.029					
Molybdenum	0.017	0.0059	0.0056	0.007	0.026				0.073	0.07
<i>PAHs</i>										
Naphthalene		0.05	0.0021			0.001			0.0011	
Acenaphthylene		0.017				0.001				
Phenanthrene		0.017	0.001		18 ³	0.001			0.0004	

<i>Other organics</i>										
Trichloromethane		0.0061				0.0025			0.0018	
Bromodichloromethane		0.0055				0.0025	0.046	0.00056		
Chlorodibromomethane		0.0036				0.0025	0.034	0.00041		
Benzene	0.25	0.045	0.0057			0.0025	0.071	0.0012	0.37	0.01
Toluene	0.73	0.013				0.005			0.002	0.8
Ethylbenzene	0.22	0.0035				0.0025	29	3.1	0.09	0.3
m + p Xylene	0.0083	0.003				0.0025				
total cyanide	0.051	0.07	0.021			0.01	0.022	0.0052	0.005	0.08
Bis(2-ethylhexyl)phthalate			0.029	0.061		0.02			0.016	0.009
Styrene	0.5	0.044	0.027	0.0041		0.0025			0.072	
Isopropylbenzene	0.0072					0.0025				
1,2,4-Trimethylbenzene	0.0048					0.0025				
4-Isopropyltoluene			0.0096			0.0025				
acetaldehyde	0.029	0.059				-- ²				
Acrylonitrile	0.105					-- ²	0.00066	0.000059		
Methyl methacrylate	0.096	0.032				-- ²				
alpha-methyl styrene	0.194					-- ²				
Methyl acetate		0.036				-- ²				
MEK		0.048				-- ²				
Isocineole			0.081			-- ²				
1,8-cineole			0.095			-- ²				
pH	No sample	6.7	11.5	10.5	6.6					
Conductivity	No sample	340	130	220	26					
unidentified compounds				0.061						

¹ Courtesy of Bill Butzbach, Chris Napier, and Tony Haggarty of the New Zealand Fire Service and Dr Harry VanEnkevort at Agriquality New Zealand.

² These eight analytes were peaks outside the standard analysis that were found and determined, however, internal standards for these samples were not run, so a determination of LOD was not possible.

³ The phenanthrene was found in the upper oily layer of this runoff. The upper layer constituted about 5% of the sample volume. LOD = Limit of Detection; blank cells indicate that the analyte was not detected.

Table 2. Compounds analysed for, but not detected in the above fire runoff:

Benzo[a]pyrene	Dibenz[a,h]anthracene	1,3,5-trimethylbenzene
Benz[a]anthracene	benzyl butyl phthalate	4-isopropyltoluene
Benzo[k]fluoranthene	Indeno(1,2,3-c,d)pyrene	PCB congeners 8, 28, 101, 138, 183
Benzo[g,h,l]perylene	Fluorene	Tribromomethane
Anthracene	Dimethyl phthalate	o-xylene
Chrysene	Diethylphthalate	di-n-butylphthalate
Fluoranthene	bis(2-ethylhexyl)adipate	n-propylbenzene
Benzo[b]fluoranthene	tert-butylbenzene	sec-butylbenzene
Pyrene	n-butylbenzene	

Fire suppressant foams were not used at any of the fires.

Cyanide was found in a fairly narrow range of concentrations in runoff from all but the house fire and autoshop fires. The concentrations found were two- to three fold higher than ecotoxicity water criteria in the vehicle and fruit shop fires.

Table 1 shows the chronic (CCC) and acute (CMC) toxicity reference values for aquatic ecological effects. It is apparent that criteria values for protection of aquatic life are available only for a small subset of compounds likely to be found in a runoff situation.

4.3 Water quality criteria

The criteria values for protection of aquatic life are based on laboratory studies using standard test methods and test organisms (e.g. daphnia, algae, plants or fish such as the fathead minnow). These tests are usually based on short-term endpoints (e.g. 48-hour LC₅₀), with margins of safety applied to the experimental No Observed Effect Level (NOEL) to reach the criteria value. The CMC is the maximum concentration below which acute toxic effects are not expected, whereas the CCC is a chronic water standard which is expected to sustain aquatic life. The Canadian value is designed for the remediation of contaminated sites, and so is analogous to the chronic CCC value.

Table 3 provides, for each fire type, a comparison of analytical values with the corresponding acute ecological risk thresholds (CMC) or the Canadian EQG value from Table 1 if the CMC was unavailable. The hazard indices were calculated as follows:

HI = Analytical result / CMC (or CCC or EQG if CMC was not available).

Table 3. Acute ecological risks, expressed as hazard indices using the USEPA CMC value, or the Canadian EQG value as a threshold for ecotoxic effects on aquatic life.

	Acute Ecological Hazard Indices, by Chemical				
	Car	Fruit shop	Sports store	House	Auto shop
Volume of run-off	200 L	3600 L	2000 L	n.r.	> 6,000 L
<i>Metals</i>					
Cadmium	10	7.9	2.6	0.28	1.9
Lead	9.4	16.9	3.4	2.62	24.6
Arsenic	0.12	0.32	0.07	0.15	1.1
Chromium	1.63	2.75	0.63	2.63	7.5
Copper	92.3	17.7	10	9.23	169.2
Zinc	91.7	125	8.3	13.3	39.2
Nickel	0.16	0.06	0.015	0.028	0.06
Mercury		3.9			
Molybdenum	0.23	0.08	0.08	0.1	1.4
<i>Organics</i>					
Naphthalene		45.5	1.9		
Phenanthrene		42.5	2.5		45,000
Halogenated methanes		3.6			
Trichloromethane		3.4			
Bromodichloromethane		0.12			
Chlorodibromomethane		0.11			
Benzene	3.5	0.63	0.08		
Toluene	365	6.5			
Ethylbenzene	0.01	0.0001			
Styrene	6.9	0.61	0.38	0.06	
total cyanide	2.3	3.2	0.95		
Acrylonitrile	159				
2-Diethylhexylphthalate			1.8	3.8	
pH		6.7	11.5	10.5	6.6
Conductivity		340	130	220	26

n.r. not reported

4.4 Ecotoxic hazards

The hazard indices in Table 3 are based on the assumption that there is complete bioavailability of the chemicals detected. This is an overestimate of the actual hazard, as some metals are significantly less bioavailable under alkaline conditions (pH > 7.0). The runoff from 2 of the fires had pH values that were considerably above neutral.

As seen in Table 3, the profile of hazards from metal contaminants was fairly consistent between fires. Copper and zinc were two ecotoxic chemicals that exceeded hazard index thresholds in the runoff from all four fires, and by the highest margins of any other

metals. The profile of organic contaminants, on the other hand, was more variable. The most highly ecotoxic risks from organic or metal contaminants were those from the vehicular and fruit shop fires. Both of these fires had runoff with unique chemical characteristics. For example, refrigerant chemicals and the highest concentrations of polyaromatic hydrocarbons were found in the fruit shop fire, while high concentrations of plastic monomers (acrylonitrile and styrene) were found in the vehicle fire. The vehicle fire had the smallest runoff volume, so the total ecological risk is correspondingly lower. The runoff from the house fire presented the lowest contaminant risk, however, the volume of water used to extinguish the fire was not reported for this fire, and so the average of the two other structural fires was used (2,800 litres) as an approximate estimate of the true volume (Table 4).

Table 4 shows the volumes of pure water in litres that would be needed to dilute the runoff from Table 3 to concentrations that would not be considered ecotoxic according to the U.S. and Canadian criteria. This takes into consideration the estimated volume of runoff at the fire scene and assumes no evaporation, thereby providing a conservative estimate of the true runoff volume. The dilutions shown would need to take place over a 48-96 hour period in order to meet with the definition of an acute timeframe that is the basis for many of the criteria and standards for protection of aquatic life.

Table 4. Volumes needed to achieve dilution of runoff to below hazardous levels.

	Acute Ecological Hazard Indices, by Chemical				
	Car	Fruit shop	Sports store	House	Auto shop
Max. Volume of Run-off	200 L	3600 L	2000 L	n.r.	> 6,000 L
<i>Metals</i>					
Cadmium	1,800	28,000	3,200		5,400
Lead	1,680	57,240	4,800	4,536	141,600
Arsenic					600
Chromium	126	6,300		4,564	39,000
Copper	18,260	60,120	18,000	23,044	958,740
Zinc	18,140	446,400	14,600	34,440	229,200
Nickel					
Mercury		9,840			
Molybdenum					
<i>Organics</i>					
Naphthalene		160,200	1,800		
Phenanthrene		149,400	3,000		6.75 E+6
Trichloromethane		8,640			
Bromodichloromethane					
Chlorodibromomethane					
Benzene	500				
Toluene	72,800	19,800			
Ethylbenzene					
Styrene	1,180				

total cyanide	260	7,920			
Acrylonitrile	31,600				
2-Diethylhexylphthalate			1,600	7,840	
pH		6.7	11.5	10.5	6.6
maximum dilution (L) and critical contaminant	72,800 Toluene	446,400 Zinc	18,000 Copper	34,440 Zinc	6.75E+6 phenanthrene 958,700 Copper

* The autoshop fire upper layer of run-off amounted to about 5% of the total volume. This has been factored into the dilution factor calculation

It can be seen in Table 4 that the autoshop fire requires the greatest volume of uncontaminated water for dilution to achieve a safe level of chemical contaminants in the receiving water body. The contaminants driving the ecological risks from this runoff were phenanthrene and copper, followed by zinc. For phenanthrene, runoff to a nearby river or stream would mean that a flow rate of approximately 2,344 litres/minute (a medium sized stream) would be needed for the runoff to be diluted below the threshold for acute ecotoxic effects (i.e. over a 48-hour period). However, the phenanthrene was in an oily phase that was not miscible with water, so the effectiveness of dilution with water would have been lessened. The dilution of copper from that fire would have required a river with a flow rate of about 333 litres/minute over a 48 hour period, which is a small to medium sized stream.

Copper and zinc were generally the most critical runoff contaminants in the four structural fires, while the vehicular fire had high concentrations of toluene and acrylonitrile that contributed to the ecological risks in addition to that from copper and zinc. The autoshop fire oily phase was problematic for sampling, and the only compound that was detected was phenanthrene. It is highly likely that further PAHs were present in the sample at lower concentrations.

Cadmium was found in all five fires, but the levels were all 10-fold or less above the water quality criteria values. In the case of the fruit shop fire, this still amounted to a volume of 28,000 litres required for dilution of the runoff to acceptable levels.

Lead was found in all four fires, but at concentrations that were more easily diluted (i.e. less than 10-fold in three of the five fires) to meet criteria levels, in comparison with zinc and copper.

Mercury was only detected in the runoff from the fruit shop fire, and the levels were not greatly above the criteria values.

The pH values for the sports store and house fire runoffs were above the Canadian contamination remediation criteria value (EQG), in one case, the pH was almost to the point of being considered corrosive (i.e. liquids are considered corrosive if they have a

pH less than 2.0 or greater than 12.0). The high pH in these two fires would mean that the copper and zinc present would be less bioavailable. On the other hand, the fruit store, with the highest zinc and copper hazard and also the greatest volume of potential runoff, had a pH value of 6.7, which means that a considerable fraction of the metals would be bioavailable.

In all four structural fires, the distance to a nearby surface water stream was reported to be between 20 and 50 meters, which means that it is quite likely that some of the runoff would have a risk of entering the waterway. In the case of the runoff from the autoshop fire, a makeshift bund was put in place to prevent the runoff from entering the storm drain which emptied directly into a nearby estuary. While some 6,000 litres were captured and disposed of from this fire, an unknown quantity (assumed to be half on conversation with Auckland Regional Council staff) entered the drain. The runoff from at least one of the other fires also drained into a nearby sewer drain.

Subsequent heavy rains could cause the surface soil to leach runoff contaminants, especially the metals, into the nearby drains and streams.

5. Discussion

The runoff from all five sampled fires is acutely ecotoxic according to comparisons with international criteria for protection of aquatic life. While this is not necessarily surprising, the results do provide scientific estimates of the risks posed by runoff and the data illustrate the key contaminants in runoff from typical fires. In all cases, uncontaminated water volumes in the range of tens of thousands of litres, up to six million litres, would be needed to dilute the runoff to achieve benign concentrations of all pollutants. These volumes correspond to, in the worst case, the amount one might encounter with the flow rate of a small to medium sized stream over 24 - 48 hours.

The results from the metal contaminant analyses from one fire is highly consistent with the concentrations reported from the Plastimet fire in Ontario (Fowles 2000).

Of the five fires, the runoff from the autoshop fire posed the greatest ecotoxicological hazard from PAHs, copper, and zinc. The volume of water used to fight this fire was about 12,000 litres. The PAHs were present in used motor or transmission oil from the shop's waste storage tank. The high levels of copper and zinc could have originated from the auto parts as well as the structural materials in the building. Similarly, the fruit shop fire, which burned nearly to the ground, required about 3,600 litres of water to put out. Both metal and organic contaminants were high in concentration and volume in this fire, possibly due to the extent to which the structure was burnt (70-80%).

The risks to ecosystems from runoff from a larger fire, especially one in which volumes of biocidal chemicals such as pesticides or herbicides are involved, would be expected to exert a much larger acute impact on aquatic ecosystems, and could easily destroy the ecosystems of most small to medium sized streams and rivers.

In the runoff from all five fires, metal contaminants exceeding water standards were common, and although the bioavailability of these metals depends greatly on the pH and hardness of the water, their presence is of concern. Many of the metals are ubiquitous and bioaccumulative, so even though the input from a single fire may be mitigated by dilution, some of the metals would be retained in biota or sediment. It is not clear how the water quality criteria are designed to deal with this property. Most of the organic contaminants, by contrast, would be expected to break down and dissipate from the ecosystem relatively quickly, with notable exceptions being chlorinated dioxins and furans.

Chlorinated dioxins and furans have been measured in house fires and tyre fires (Steer et al., 1995; Thompson et al., 1993; Wunderli et al., 2000), although the concentrations have not been reported in runoff from typical building or house fires. These compounds were not investigated in this report. Tyre fires have unique characteristics that do not necessarily apply to the building fires sampled in the current study.

Copper and zinc appear to be key contaminants contributing to the acute ecological risks to aquatic life from fire-water runoff from ordinary fires. These compounds, while ecotoxic in their bioavailable (i.e. ionic salt) forms, especially to aquatic plant life, are of much less concern to human health, as shown by the difference in criteria values for human and ecosystem health protection in Table 1. This distinction is important to recognise as it becomes clear that criteria, such as drinking water standards, designed for the protection of human health, are not appropriate for ecosystem protection (and vice versa).

Chelated copper compounds are used commercially as biocides to control algae, not rooted aquatic plants. Most algae species are effectively controlled by these herbicides. However, copper is a toxic metal that is persistent in the environment. Copper can be toxic to fish and aquatic animals at concentrations near levels used to control algae, especially in soft water. The toxicity of copper increases as water hardness decreases.

Copper is one of the elements of greatest concern for ecosystems in urban storm water runoff (<http://home.pacbell.net/gfredlee/watershe.htm>). Copper and many other heavy metals are often present in urban storm water runoff at concentrations above U.S. EPA water quality criteria. There is a lack of solid scientific research detailing how copper comes to be found in lakes, streams, and other bodies of water generally (<http://innovations.copper.org/199904/conn.html>). However, it has been found that one of the principal sources of environmental copper is its use in brake linings/pads for some types of automobiles (<http://home.pacbell.net/gfredlee/watershe.htm>).

Levels of copper in marine water range from 0.2 to 500 µg/L while in freshwater levels range from 0.3 to 900 µg/L. The natural background level has been reported in the United States to be approximately 0.2 µg/L (<http://www.science.mcmaster.ca/Biology/4S03/COPPER.HTM#one>)

The speciation of copper is directly linked to its bioavailability and toxicity. Copper is most toxic in the free ion form prevalent at $\text{pH} < 7$. Various processes in the aquatic environment act to bind copper to inorganic and organic ligands which precipitate out of solution. Copper may also bind to particulates which settle out of the water column.

Zinc is a heavy metal used in coatings to prevent rust, in dry cell batteries, and mixed with other metals to make alloys like brass and bronze. Zinc compounds have multiple uses in paints, rubber, dye, wood preservatives, and ointments. Zinc contamination of the environment is widespread, it can be found at 801 of 1,416 EPA National Priorities List Sites. The impacts of zinc on fish can be put into three general categories. (1) Zinc can block biosynthesis of essential functional groups on certain proteins, (2) it can displace essential metals in biomolecules and (3) it may modify the active conformation of biomolecules. For salmonoids the 96-hour LC_{50} ranges from 0.05 - 7 mg/L (<http://www.science.mcmaster.ca/Biology/4S03/RL5.HTM#4>). The runoffs from the vehicle and fruit shop fires both had concentrations of Zn that exceeded this range.

In addition to its toxicity to fish, soluble zinc used as a positive control in toxicity testing for some aquatic plants, according to USEPA aquatic toxicity testing guidelines (http://www.epa.gov/docs/OPPTS_Harmonized/850_Ecological_Effects_Test_Guidelines/Drafts/850-4400.txt.html).

Both copper and zinc will be found in high concentrations in runoff from building fires, and apparently also from vehicular fires. This is probably due to ash contaminated with metals from the galvanised iron fixtures and copper piping present in buildings. Residual mineral content from organic fibres may also contribute to the metals in runoff.

6. Conclusions

Runoff from even small commonly encountered fires poses a toxic threat to aquatic ecosystems. The results from the monitoring of 4 structural fires and 1 vehicular fire in this study are consistent with the runoff concentrations from different types of fires reported in other countries. The runoff from the autoshop fire was the most hazardous to aquatic life. In one case, a fire at a fruit shop yielded runoff with metal concentrations comparable to that found in a large industrial plastics warehouse fire (the Plastimet fire) in Ontario, although the volumes of runoff for the fruit shop fire were almost certainly much smaller. The runoff from the house fire presented the lowest ecotoxic hazard.

Undiluted, the runoff from all five fires would be acutely lethal to aquatic life, if it is assumed that even a fraction of the contaminants are bioavailable. The most significant and consistent contributors to ecotoxic hazards across the five fires were copper and zinc.

The experience of ecosystems impacted by similar fires overseas indicates that the metal concentrations dissipate from the surface water within several days and do not pose a chronic hazard. It does appear therefore, that in most cases, the threat of lasting ecological damage is small, provided that the receiving waterway is of sufficient size and flow rate to reduce the acute impacts.

No fires at chemical storage or other heavy industrial sites were available for sampling in the time period, but it is highly likely that runoff from fires at such facilities would be much more of a toxic threat than those fires in this report and could result in ecological catastrophe for the aquatic life in the receiving waterway.

7. References

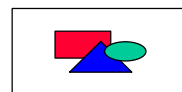
Fowles J. 2000. Literature review on the ecotoxic effects of fire-water runoff. A report by the Institute of Environmental Science and Research to the New Zealand Fire Service. November 2000.

Steer PJ, Tashiro CHM, McIllveen WD, and Clement RE. 1995. PCDD and PCDF in air, soil, vegetation, and oily runoff from a tire fire. *Water, air and soil pollution* 82:659-674.

Thompson TS, Kolic TM, Townsend JA, and Mercer RS. 1993. Determination of polychlorinated dibenzo-p-dioxins and dibenzofurans in tire fire runoff oil. *J. Chromatography* 648:213-219.

Wunderli S, Zennegg M, Dolezal IS, Gujer E, Moser U, Wolfensberger M, Hasler P, Noger D, Studer C, and Karlaganis G. 2000. Determination of polychlorinated dibenzo-p-dioxins and dibenzo-furans in solid residues from wood combustion by HRGC/HRMS. *Chemosphere* 40:641-649.

Appendix A: Questionnaire and Data Sheet



ECOTOXIC EFFECTS OF FIRE RUN-OFF

DATE _____

NAME _____

ADDRESS of FIRE _____

Local Authority/Fire Department doing sampling _____

Fire Setting: Type of fire (tick if applicable):

House		Small business	
Apartment building		Non-building	
Warehouse/storage facility		Tire	
Manufacturing plant		Vehicle	
School/public building		Other	

If "other" or "non-building", specify: _____

Fire Details:

**1. Time firefighting material use (water, foam, etc) started _____,
Time of Sampling _____**

2. Building contents of concern (i.e. chemical stores – pesticides, petroleum products)

Materials used to fight fire (e.g. foams), if other than water. Estimate volume.

Materials:

Volumes:

4. Flow rate of water used (*approximate*), and duration of use

Rate =

Duration =

5. Estimated total volume of water used (*litres*)

6. Extent of burn damage to structure and contents at time of sampling (%)
