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Contamination of water supplies by volcanic ashfall: A literature review and simple impact modelling

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Abstract

Volcanic ash is the most widely-distributed product of explosive volcanic eruptions, and can disrupt vital infrastructure on a large scale. Previous studies of effects of ashfall on natural waters and water supplies have focused mainly on the consequences of increased levels of turbidity (ash suspended in water), acidity and fluoride, with very little attention paid to other contaminants associated with volcanic ash. The aims of this paper are twofold: firstly, to review previous studies of the effects of volcanic ashfall on water supplies and identify information gaps; and secondly, to propose a simple model for predicting effects of ashfall on water supplies using available information on ash composition.

We reviewed reported impacts of historic eruptions on water supplies, drawing on case studies from New Zealand, Vanuatu, Argentina, the USA, Costa Rica, Montserrat, Iceland and Guadeloupe. Elevated concentrations of fluoride, iron, sulphate and chloride, as well as turbidity and acidity, have been reported in water supplies. From a public health perspective, the two main issues appear to be: (1) outbreaks of infectious disease caused by the inhibition of disinfection by high levels of suspended ash, and (2) elevated fluoride concentrations.

We devised a simple model using volcanic ash leachate composition data to predict effects on receiving waters. Applying this model to the effects of Ruapehu ash, from the 1995/1996 eruptions, suggests that the primary effects of concern are likely to be an increase in acidity (decrease in pH), and increases in concentrations of the metals aluminium, iron and manganese. These metals are not normally considered to pose health risks, and are regulated only by secondary, non-enforceable guidelines. However, exceedences of guideline values for Al, Mn, Fe and pH will cause water to become undrinkable due to a bitter metallic taste and dark colour, and may also cause corrosion, staining and scale deposition problems in water tanks and pipes. Therefore, the main issues following volcanic ashfall of similar composition to Ruapehu ash are likely to be shortages of potable water and damage to distribution systems, rather than risks to public health.

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1. Introduction

Volcanic ash is the most widely-distributed product of explosive volcanic eruptions, and areas hundreds of kilometres distant from an erupting volcano can receive ashfalls. Even minor quantities of ash can disrupt infrastructure such as transport networks, electricity and water supplies and stormwater and sewerage systems (Blong, 1984; Johnston et al., 2000). During the 1995–1996 eruptions of Ruapehu, in New Zealand, contamination of water supplies was a common concern in communities affected by ashfall (Johnston, 1997a; Johnston et al., 2000). Authorities were generally unable to allay public fears because of a lack of supporting information on specific effects of volcanic ashfall on water supplies, including considerations such as the quantity of ashfall necessary to produce adverse effects, and the specific nature of contaminants that may pose a health risk to consumers or otherwise compromise the integrity of water supplies.

There is considerable information available on the composition of volcanic ash leachates. A recent review by Witham et al. (2005) summarise results of over 55 studies reporting ash leachate data for 27 volcanoes. Over 55 soluble components have been detected; those occurring at the highest concentrations are sodium, calcium, magnesium, chloride, sulphate and fluoride. Volcanic ash leachates are also known to be highly acidic, due to the presence of strong mineral acids. Previous studies of the effects of ashfall on natural waters and water supplies have focused mainly on the consequences of increased levels of turbidity (ash suspended in water), acidity and fluoride, with very little attention paid to other contaminating elements associated with volcanic ash (Collins, 1978; Oskarsson, 1980; Weniger et al., 1983; Smithsonian Institution, 1997; Cronin and Sharp, 2002).

This paper has two main aims: firstly, to review previous studies of the effects of volcanic ashfall on water supplies and identify information gaps; secondly, to propose a model for predicting ashfall effects on water supplies using available information on ash composition. Some applications of this model are demonstrated, along with a critical discussion of its strengths and limitations.

2. Impacts of volcanic ash on water supplies

Impacts on water supplies have been reported subsequent to a number of historic eruptions. We have reviewed studies describing these impacts on a case-by-case basis (Johnston et al., 2004). The main findings are summarised in Table 1, and more fully below. Also

provided, for comparison, are drinking water standards prescribed by the United States Environmental Protection Agency, the World Health Organisation, the New Zealand Ministry of Health and the Japanese Ministry of Health, Labour and Welfare (Table 2). Drinking water quality is commonly regulated using a two-tier system. Primary standards are legally enforceable limits set for contaminants posing a health risk. Secondary standards are non-enforceable guideline values for contaminants which are not known to be a health risk but which make drinking water unacceptable to consumers because of aesthetic factors such as taste, colour or odour, or effects on the supply system such as staining or scale deposition.

2.1. Turbidity

A commonly-reported water contamination problem (e.g. Wilcox, 1959; Collins, 1978; Warrick et al., 1981; Blong, 1984) is an increase in turbidity due to the suspension of ash in water. Turbidity (measured in Nephelometric Turbidity Units, or NTU) is a measure of the cloudiness of water, and is caused by suspended particulate matter. It has no health effects in itself, but particulates can protect micro-organisms from the effects of disinfection and can stimulate bacterial growth. Effective water treatment, including terminal disinfection, depends on the control of turbidity. Some regulatory approaches to the control of turbidity are shown in Table 3.

The suspension of volcanic ash in water can easily exceed acceptable limits for turbidity. Following the May 1980 eruption of Mt St Helens in the USA, increases in the occurrence of waterborne *Giardiasis* were reported for months afterwards, as far away as Montana. These events were linked to heavy rainfall washing the deposited ash into water supplies (Weniger et al., 1983).

2.2. Acidification

Surface coatings on fresh volcanic ash are highly acidic, due to the influence in the plume of aerosols composed of the strong mineral acids H_2SO_4 , HCl and HF . Therefore, when freshly-erupted ash comes into contact with water, it has the potential to lower the pH beyond acceptable limits for drinking water supplies (Table 2) or for the protection of aquatic life. The World Health Organisation (WHO, 2004) considers the potability of water likely to be markedly impaired below pH 6.5. Low pH water is also likely to be plumbosolvent, particularly if it is also soft (containing low levels of calcium and magnesium). These properties can give the water a high solvation potential, so that plumbosolvent

Table 1

Review of historic impacts on water supplies from volcanic ash: summary of main impacts

Impact	Comment	Examples	Reference
Physical impacts of ash	<ul style="list-style-type: none"> • Ash can clog intake structures • Abrasive nature of ash can cause increased wear on equipment 	Irazú, Costa Rica (1963) Fine ash clogged filters at the intake to San José's river-fed water supply. Water had to be trucked in.	Blong (1984)
	<ul style="list-style-type: none"> • Corrosive nature of ash can damage electrical equipment and corrode metallic structures such as pipes 	Mt Ruapehu, New Zealand (1995/96) Rotorua's water supply cut when resident washed ash into a power transformer and cut electricity supply to pumps.	Johnston (1997a)
Water shortages	<ul style="list-style-type: none"> • Heavy demands on water for clean-up of ashfall 	Mt Spurr Volcano, Alaska (1992) City of Anchorage experienced severe water shortages because of demand for ash cleanup; one reservoir completely emptied; no water available for firefighting.	Johnston (1997b)
Increased turbidity	<ul style="list-style-type: none"> • Suspension of ash in water increases turbidity; this can make water undrinkable and compromise terminal disinfection 	Mt St Helens, USA (1980) Increased occurrence of waterborne <i>Giardiasis</i> due to turbidity from volcanic ash inhibiting disinfection.	Weniger et al. (1983)
Acidification	<ul style="list-style-type: none"> • Surface coatings on fresh ash are highly acidic, due to adsorbed volcanic aerosols H₂SO₄, HCl, HF 	Copahue Volcano, Argentina (2000) pH 2.1 reported in nearby Lake Caviahue; pH 2.5 reported in streams 60 km from source.	Smithsonian Institution (2000)
Fluoride contamination	<ul style="list-style-type: none"> • Fluoride from HF readily leached from fresh ash; can exceed safe limits for people and animals 	Lopevi, Vanuatu (2003) 10 mg/L fluoride reported in rainwater-fed tanks. Hekla, Iceland (1947–1948) 9.5 mg/L fluoride recorded in Merkjá stream.	Cronin et al. (2003b) Stefánsson and Sigurjónsson (1957)
Other contaminants	<ul style="list-style-type: none"> • Freshly-fallen ash releases soluble components into receiving waters • Many studies made of ashfall leachates, but few have focused on receiving waters 	Copahue Volcano, Argentina (2000) Increased concentrations of iron, fluoride, sulphate in water supplies.	Smithsonian Institution (2000)
	<ul style="list-style-type: none"> • Major leachate components: sulphate, Cl, Na, Ca, Mg, F • Minor leachate components: Mn, Zn, Ba, Se, Br, B, Al, Si, Cd, Pb, As, Cu, Fe 	Soufrière Hills, Montserrat (1997) Increased concentrations of sulphate, chloride and fluoride.	Smithsonian Institution (1997)

waters have the potential to dissolve metals from plumbing fittings.

There are many examples of the acidification of natural waters and water supplies following volcanic ashfall. The 1969 Ruapehu eruptions deposited 6–7 mm of ash over the western flanks of the mountain, contaminating water supplies (Collins, 1978). At Iwikau village, located at the base of Whakapapa skifield, pH levels ranging from 4.4 to 6.0 were recorded in roof tank supplies. Further down the mountain, Whakapapa Village received 1–6 mm of ash; the pH of its stream-fed water supply was recorded as 5.6. Similar pH levels in receiving waters following volcanic ashfall have been reported in many other studies (e.g. Wilcox, 1959; Smithsonian Institution, 1997; Cronin and Sharp, 2002). Very low pH values are associated with the greatest thicknesses of ashfall. The July 2000 eruptions of Copahue volcano in Argentina deposited 30–50 mm of ash into and around Lake Caviahue. Water authorities in the area reported colour changes from the normal deep blue to greyish-green. In the weeks following the eruption,

the pH of the lake dropped to 2.1. Even at a distance of 60 km, ashfall increased turbidity in streams and decreased the pH to 2.5 (Smithsonian Institution, 2000). However, it should be noted that the composition of Lake Caviahue is thought to be influenced by acid hot springs. These feed the Upper Rio Agrio river system, which discharges into Lake Caviahue (Varekamp, 2004). Thus, the acidification observed in July 2000 was probably only partially due to ashfall.

2.3. Fluoride and other soluble contaminants

The existence of readily water-soluble material on fresh volcanic ash has been documented in many studies, with a recent, comprehensive review now available (Witham et al., 2005). Over 55 soluble components have been reported in volcanic ash leachates, with the anions Cl[−], SO₄^{2−} and F[−] and the cations Ca²⁺, Na⁺ and Mg²⁺ generally occurring at the highest concentrations.

Witham et al. (2005) describe fluoride (F[−]) as the principal toxic element adsorbed on ash, and suggest that

Table 2

A comparison of drinking water standards (concentrations in mg/L)

		USEPA ^a	WHO ^b	New Zealand ^c	Japan ^d	Potential effects if standard exceeded ^e
		Primary standards (MCLs)	Secondary standards	Health standards	Aesthetic MAVs GVs	
<i>Elements of health significance</i>						
Antimony	Sb	0.006		0.02	0.02	Increase in blood cholesterol; decrease in blood sugar
Arsenic	As	0.01		0.01		Skin damage, increased cancer risk
Barium	Ba	2		0.7	0.7	Hypertension
Boron	B			0.5	1.4	May affect male reproductive tract
Bromate ^f	Br	0.01		0.01	0.01	Increased cancer risk
Cadmium	Cd	0.005		0.003	0.004	Kidney damage
Chromium	Cr	0.1		0.05	0.05	Allergic dermatitis
Copper	Cu	2		2	2	Liver or kidney damage
Fluoride	F	4		1.5	1.5	Dental and skeletal fluorosis
Lead	Pb	0.015		0.01	0.01	Impairs development and learning in children
Lithium	Li				1	g
Molybdenum	Mo			0.07	0.07	g
Mercury	Hg	0.002		0.001	0.002	Kidney damage
Nickel	Ni			0.02	0.02	g
Nitrate	NO ₃	44.3		50	50	Can cause blue-baby syndrome in infants
Selenium	Se	0.05		0.01	0.01	Liver or kidney damage; damage to circulation and nervous systems
Thallium	Tl	0.002				Blood, kidney, liver or intestine problems
<i>Elements influencing drinking water acceptability</i>						
Acidity	H ⁺		pH 6.5–8.5	pH 7–8.5	pH 5.8–8.6	Low pH: bitter metallic taste, corrosion High pH: soapy feel, soda taste
Aluminium	Al		0.05–0.2	0.1	0.2	Floc deposits, discolouration
Chloride	Cl		250	250	200	Salty taste
Copper	Cu		1	1	1	Metallic taste, blue-green staining
Hardness	Ca +Mg			200	300	Scale deposits and scum formation
Iron	Fe		0.3	0.2	0.3	Rusty colour, metallic taste, red staining
Manganese	Mn		0.05	0.04	0.05	Black or brown colour, black staining, bitter metallic taste
Sodium	Na			200	200	Salty taste
Sulphate	SO ₄		250	250		Salty taste
Zinc	Zn		5	1.5	1	Metallic taste

g No information available.

^a The United States Environmental Protection Agency has a two-tier system for the regulation of drinking water quality. The National Primary Drinking Water Standards set Maximum Contaminant Levels (MCLs) that are legally enforceable, for the protection of public health. The National Secondary Drinking Water Regulations are non-enforceable guidelines regulating contaminants that may cause cosmetic or aesthetic effects but are not a health risk. See EPA (2002).

^b The World Health Organisation defines guideline values for a range of chemicals of health significance. No formal guidelines have been set for chemicals affecting the acceptability of drinking water, though a discussion of concentration values required to meet acceptability criteria is provided. See WHO (2004).

^c The Drinking Water Standards for New Zealand 2005 set Maximum Acceptable Values (MAVs) for determinands of health significance. Guideline Values (GVs) have been set for aesthetic determinands (similar to acceptability determinands). See MOH (2005).

^d One set of drinking water quality standards have been established for Japan, by the Ministry of Health, Labour and Welfare. See <http://www.jwwa.or.jp/frame-e02.html>.

^e Discussion based on information provided by USEPA.

^f Bromate is a disinfection by-product following ozonation.

future eruptions of six volcanoes (Avacha, Galunggung, Grimsvotn, Hekla, Lonquimay and Ruapehu) be monitored to assess hazards from this element, on the basis of available ash leachate data.

After the 1947–48 eruption of Hekla in Iceland, a survey of rivers and streams in the vicinity showed temporarily elevated fluoride concentrations, of up to 9.5 mg/L in Merkjá stream (Stefánsson and Sigurjónsson,

Table 3
Approaches to the regulation of turbidity in drinking water

Regulatory authority	Type of standard	Approach
USEPA	Primary standard	From 1 January 2002, turbidity in raw drinking water may never exceed 1 NTU, and 95% of daily samples in any month must be less than 0.3 NTU.
WHO	Secondary standard	No formal guideline set, but median turbidity <0.1 NTU is recommended for effective disinfection.
New Zealand MOH	Secondary standard	Median turbidity should be <1 NTU and no samples should exceed 5 NTU. 2.5 NTU recommended to protect appearance of drinking water.

1957). Fluoride levels in drinking water supplies were lower and did not exceed 1.6 mg/L, probably because most water supplies were from underground sources or were covered. Following a 2003 eruption from Lopevi volcano, on Vanuatu, rainfall-fed water tanks were elevated from pre-event values of 0.4–0.7 mg/L fluoride to 1.3–2.7 mg/L under 1 mm ash, and to 10 mg/L under 3 mm ash (Cronin et al., 2003b). At Ruapehu volcano in New Zealand, a level of 6 mg/L fluoride was reported in roof tank water supplies in Iwikau Village during the 1969 eruptions (Collins, 1978). These values exceed the World Health Organisation's primary drinking water standard for fluoride of 1.5 mg/L (Table 2). However, it is important to note that in the above cases, contamination episodes were short-lived. Short-term incursions over primary standards may not necessarily be of concern because drinking water standards for chemical contaminants refer to risks associated with long-term consumption.

Possibly of greater concern is chronic contamination of water supplies by ashfall due to intermittent or semi-continuous volcanic activity, such as that observed on the islands of Tanna and Ambrym in Vanuatu. Cronin and Sharp (2002) reported levels of up to 2.8 mg/L fluoride in rainwater tanks in villages downwind of the active vents on Ambrym. Following small ash-eruptions in 2005 on Ambrym, the mean fluoride content of over 180 rainwater tanks was elevated from approximately 1.0–1.5 mg/L to 4.1 mg/L, with some tanks containing concentrations of >10 mg/L fluoride (Crimp et al., 2005). These levels, consumed on a long-term basis, are thought to cause dental fluorosis (Crimp et al., 2005).

Other exposure routes for fluoride may also be important, such as the dietary intake of ash-coated crops, pasture or soil. These are thought to be particularly important for livestock. Following historic eruptions in Iceland and Chile, fluorosis has been the most common

cause of stock poisoning (Sigurðsson and Pálsson, 1957; Thorarinnsson, 1979; Oskarsson, 1980; Arya et al., 1990). The deaths of several thousand sheep after eruptions of Ruapehu on 11 and 14 October 1995 were attributed to fluorosis (Cronin et al., 2003a).

Other than fluoride and acidity, little attention has been paid to contamination of water supplies by other soluble components of ashfall. There are some reports of elevated levels of iron, sulphate and chloride (e.g. Smithsonian Institution, 1997, 2000; Cronin and Sharp, 2002; Baxter and Ancia, 2002) but little or no discussion of implications for drinking water quality.

2.4. Physical impacts of ash

Ash can cause physical damage to water treatment plants. Ash suspended in rivers or lakes can block intake structures; the 1963 eruption of Irazú in Costa Rica caused fine ash to clog filters at the intake to the capital city's river-fed water supply. As a result, water needed to be brought in by truck to San José (Blong, 1984). Because of its highly abrasive and corrosive nature, ash can damage intake structures and increase levels of wear on other plant or machinery it comes into contact with. Ash washed into the upper Tongariro river during the 1995/1996 Ruapehu eruptions caused considerable abrasion damage to turbines at the Rangipo hydroelectric power station (Malcolm and van Rossen, 1997). Ashfalls were widespread over much of the North Island during 1995/1996. The city of Rotorua, approximately 150 km NNE of Ruapehu, constructed enclosures over the city's supply springs to protect them from ashfall; this proved worthwhile on 17 June 1996 when ash fell on Rotorua. However, Rotorua almost ran out of water when a resident washed ash into a power transformer which exploded, cutting electricity to water pumps (Johnston, 1997a). Ashfall damage caused power outages to water treatment plants and cut off drinking water supplies following the July 2000 eruption of Mt Copahue volcano, Argentina (Smithsonian Institution, 2000).

2.5. Water shortages

Other indirect problems can occur as a result of increased water demand by residents of communities affected by ashfalls as cleanup takes place. The August 1992 eruption of Mt Spurr volcano, Alaska, deposited about 3 mm of ash on the city of Anchorage. The cleanup of ash resulted in excessive demands for water, increasing the peak demand by 70%. This in turn caused widespread pressure and supply problems which led to several storage reservoirs dropping to dangerously low levels,

and at least one reservoir being completely emptied, with insufficient reserves for firefighting had they been required (Johnston, 1997b; Johnston et al., 2004).

In summary, volcanic ashfall can have serious effects on drinking water supplies. These include physical blockages of intake structures by ash, and damage due to abrasion or corrosion of equipment. Suspension of ash in water increases levels of turbidity, acidity and soluble components. The major public health concerns are thought to be the potential for outbreaks of waterborne infectious diseases due to the inhibition of disinfection at high levels of turbidity, and elevated concentrations of fluoride increasing risks of dental and skeletal fluorosis. Physical impacts of ash, and problems due to high levels of acidity, turbidity and fluoride are well-documented. However, little attention has been paid to other soluble components of volcanic ash, and their potential consequences for water supplies.

3. Modelling chemical contamination in receiving waters

The potential for contamination of water supplies or surface waters by volcanic ashfall will depend on: the composition of the ash, the quantity of ashfall, and the volume of water available for dilution of the soluble components. We derived a simple model to predict concentration increases in receiving waters due to leaching from ashfall. This model can be concisely expressed as follows:

$$C_{\text{water}} = C_{\text{ash}} TDA/V \quad (1)$$

where C_{water} is the expected concentration increase of a soluble contaminant in the receiving water body in mg/L, C_{ash} is the concentration of the contaminant in the ash in mg/kg, T is the thickness of the ash in metres, D is the density of ash in kg/L, A is the surface or catchment area of the supply in square metres and V is the volume of the receiving water in cubic metres.

It should be noted that the model predicts concentration *increases* in receiving waters, rather than final concentrations. This is because the water-soluble components of volcanic ash are also present in natural waters.

The model cannot, in general, be used to predict pH changes, because natural waters have varying levels of capacity to neutralise added acid (this property is known as *alkalinity*). Alkalinity in most natural waters is primarily due to the presence of carbonate (CO_3^{2-}) and bicarbonate (HCO_3^-) ions (Andrews et al., 1996). Furthermore, solid-phase reactions (for instance, with lake sediments or concrete walls of water tanks) can also buffer pH.

However, unpolluted rainwater has very low levels of alkalinity, and is slightly acidic (pH 5.6) due to the dissolution of atmospheric carbon dioxide and subsequent formation of carbonic acid (H_2CO_3), which is weakly acidic (Andrews et al., 1996). Because rain-fed water supplies stored in non-concrete tanks are expected to have very low levels of alkalinity, the model may therefore be able to make realistic predictions of pH changes following volcanic ashfall for this situation.

3.1. Application of model

The 1995/1996 eruptions of Ruapehu provide a useful basis for demonstrating this model. Mt Ruapehu, located at the southern end of the Taupo Volcanic Zone in the North Island of New Zealand, is an active andesitic volcano which has erupted more than 100 times in the last 135 years (Houghton et al., 1987; Cronin et al., 1998). Eruptions of the size of the most recent 1995/1996 events are considered to have a return period of approximately 50–100 years; eruptions of similar size occurred in 1945 and distributed similar quantities of ash over the North Island. Ashfall from the 1995/1996 eruptions was well-characterised with respect to leachate composition (Christenson, 2000; Cronin et al., 1998, 2003a).

To illustrate the use of the model, the following scenarios have been chosen:

- (1) Effects of Ruapehu ash on a domestic rainwater tank in a rural area close to Mt Ruapehu;
- (2) Effects of Ruapehu ash on Auckland's potable water supply.

3.2. Model input parameters

3.2.1. Contamination potential A/V and ash thickness T

The quantity A/V can be defined as the contamination potential (with units of m^{-1}) for a particular water body. A water body with a small volume and relatively large catchment area, such as a domestic rainwater tank, will have a correspondingly high contamination potential. A deep lake will have a lower contamination potential than a shallow lake with the same surface area, because of the increased volume of water available for dilution.

Many households in rural areas of New Zealand use rainwater tanks for their domestic water supply. A typical system (based on a known example) might have a roof catchment area of 176 m^2 and a rainwater tank of 13.5 m^3 capacity. This gives a contamination potential A/V of 13.0 m^{-1} . For these calculations, ash thicknesses of 1, 5 and 10 mm have been used. During the 1995/1996

eruptions of Ruapehu, ashfalls of 10 mm were confined to within a few kilometre downwind of Ruapehu, but ashfalls of 1 mm were recorded over much larger areas extending over 200 km from the volcano (Cronin et al., 1998).

Auckland is New Zealand's largest city, with a population of over 1.2 million in the Greater Auckland region. The city's water supply is derived primarily from ten reservoirs located in the Waitakere Ranges west of Auckland, and the Hunua Ranges to the southeast. Auckland is located within one of New Zealand's most recently active volcanic fields. In addition, it is now recognised that the region is threatened by other active volcanic centres, including Taupo, Okataina, Tongariro and Taranaki. During the 1995/1996 eruptions of Ruapehu, trace amounts of ash were deposited on Auckland on 17 June 1996, closing Auckland International Airport. The deposition of 1–2 mm ash on Auckland (considering not only Ruapehu but other volcanic centres) is estimated to be a 1 in 100 year event (Johnston et al., 2004). Ash thicknesses of 1 and 5 mm have been used in these calculations.

To represent effects on Auckland's water supplies, the model (Eq. (1)) has been applied to the Upper Mangatawhiri reservoir, located in the Hunua ranges. It is the second largest of the ten reservoirs, and contains 17% of the total storage capacity. Values of A/V for this reservoir, shown in Table 4, vary by a factor of approximately 50 depending on the storage level in the reservoir, and whether ashfall from the entire catchment is assumed to run off into the reservoir, or only the ashfall deposited directly on the reservoir surface is assumed to contribute. The maximum A/V value of 4.54 m^{-1} assumes that ashfall from the entire catchment is washed into the reservoir while it is at minimum storage capacity. This is unlikely because there is likely to be at least partial retention of ashfall solutes on soils within the catchment, and also because the heavy rainfall necessary to wash the ash rapidly into the reservoir would increase the storage volume. The minimum A/V value of 0.08 m^{-1} refers to a

situation where ashfall is deposited onto the surface of the reservoir while at maximum storage volume, followed by dry weather conditions during which little or no ash is washed in from the catchment.

In practice it is very difficult to predict a value of A/V for a particular reservoir. For demonstration purposes, a value of $A/V = 0.13 \text{ m}^{-1}$ has been chosen to represent an ashfall event occurring during dry weather. In this scenario, water levels would be expected to be low, and ashfall from the catchment not washed into the reservoir. This value of A/V is at the lower end of the range shown in Table 4, but has been chosen because it represents a realistic situation.

3.2.2. Ash composition C_{ash}

Ashfall from the 1995/1996 eruptions of Ruapehu was characterised with respect to its soluble components (Cronin et al., 1998; Christenson, 2000; Cronin et al., 2003a). The study by Cronin et al. (1998) has been used as the primary source of data on Ruapehu ash composition as the most complete set of elements has been measured, and the methods used are the most appropriate according to the recommendations of Witham et al. (2005). These data have been supplemented where necessary from Cronin et al. (2003a), Christenson (2000), Armienta et al. (1998), Smith et al. (1983) and Witham et al. (2005). These latter three studies provide data on leachable concentrations of antimony, barium, mercury and thallium in volcanic ash. These elements were not measured in Ruapehu ashfall, but legally enforceable primary standards have been set for them in drinking water.

3.2.3. Density

Reported dry bulk densities of newly fallen and slightly compacted ashfall deposits range from 500–1500 kg/m^3 (Kienle, 1980; Moen and McLucas, 1980; Scott and McGimsey, 1994; Cronin et al., 1998). For these calculations, a mid-range value of 1000 kg/m^3 ($=1 \text{ kg/L}$) has been used.

3.3. Predicted concentration increases

Predicted concentration increases in receiving waters as a result of volcanic ashfall from an eruption of Ruapehu are shown in Table 5. Exceedences of drinking water standards (Table 2) are shown by dark shading; light shading indicates predicted concentration increases which exceed 50% of guideline values. These are of interest because leaching of soluble components may increase existing concentrations above guideline levels. For instance, if a raw water supply contains 1 mg/L fluoride, ashfall increasing the concentration of fluoride by 0.8 mg/L

Table 4

Range of contamination potential (A/V) values for Upper Mangatawhiri reservoir^a, Hunua Ranges, Auckland

	Contamination potential A/V	
	Maximum storage	Minimum storage
Whole catchment	1.59	4.54
Reservoir surface area only	0.08	0.13

^a Upper Mangatawhiri reservoir has a capacity of 16,224,000 m^3 , a catchment area of 2580 ha and a surface area of 128.5 ha. The minimum storage volume is assumed to be 35% of the maximum storage (Johnston et al., 2004).

Table 5

Predicted concentration increases (C_{water}) in receiving waters with different thicknesses of volcanic ashfall

C_{ash} (mg/kg) ^a			C_{water} (mg/L) for domestic rainwater tank			C_{water} (mg/L) for Upper Mangatawhiri reservoir	
Ash thickness			1 mm ash	5 mm ash	10 mm ash	1 mm ash	5 mm ash
A/V ^b			13	13	13	0.13	0.13
<i>Elements of health significance</i>							
Antimony ^c	Sb	0.07	0.00091	0.0046	0.0091	9.1E-06	4.6E-05
Arsenic	As	0.032	0.00042	0.0021	0.0042	4.2E-06	2.1E-05
Barium ^d	Ba	0.152	0.0020	0.0099	0.020	2.0E-05	9.9E-05
Boron	B	2.6	0.034	0.17	0.34	0.00034	0.0017
Cadmium	Cd	0.0038	5.0E-05	2.5E-04	5.0E-04	4.9E-07	2.5E-06
Chromium	Cr	0.044	0.00057	0.0029	0.0057	5.7E-06	2.9E-05
Copper	Cu	4	0.052	0.26	0.521	0.00052	0.0026
Fluoride	F	86	1.12 ^e	5.6	1.2	0.011	0.056
Lead	Pb	0.0014	1.8E-05	9.1E-05	1.8E-04	1.8E-07	9.1E-07
Lithium	Li	0.19	0.0025	0.012	0.025	2.5E-05	0.00012
Molybdenum	Mo	<0.001	<1.3E-05	<6.5E-05	<0.00013	<1.3E-07	<6.5E-07
Mercury ^f	Hg	0.0087	0.00011	0.00057	0.00113	1.1E-06	5.7E-06
Nickel	Ni	0.35	0.0046	0.023	0.046	4.6E-05	0.00023
Nitrate	NO ₃	25.6	0.33	1.7	3.3	0.0033	0.017
Selenium	Se	0.1	0.0013	0.0065	0.013	0.000013	0.000065
Thallium ^g	TIB	0.073	0.00095	0.0048	0.0095	9.5E-06	4.7E-05
<i>Elements influencing drinking water acceptability</i>							
Acidity ^h	H ₊	0.00041	5.3E-06	2.7E-05	5.3E-05	–	–
	pH		5.27	4.57	4.27	–	–
Aluminium	Al	195	2.5	13	25	0.025	0.13
Chloride	Cl	85	1.1	5.5	11.1	0.011	0.055
Copper	Cu	4	0.052	0.26	0.52	0.00052	0.0026
Hardness ⁱ	Ca+Mg	15, 200	198	990	1980	2.0	9.9
Iron	Fe	46	0.60	3.0	6.0	0.0060	0.030
Manganese	Mn	14.3	0.19	0.93	1.9	0.0019	0.0093
Sodium	Na	413	5.4	27	54	0.054	0.27
Sulphate	SO ₄	5722	75	373	746	0.74	3.7
Zinc	Zn	5.6	0.073	0.37	0.73	0.00073	0.0036

^a Ruapehu ash composition data are primarily derived from Cronin et al. (1998) with supplementary data from Christenson (2000).^b A/V is the contamination potential of a waterbody, and has units of m₋₁ (surface area divided by volume).^c Antimony value is from Armienta et al. (1998) for Popocatepetl and is a mean of 11 data points excluding one outlier.^d Barium value is from Smith et al. (1983) for Mt St Helens.^e Dark shading refers to exceedences of the DWSNZ 2005 (shown in Table 2). Light shading refers to C_{water} values which exceed 50% of these standards. The USEPA primary MCL value for thallium has been used as there is no standard for this element in New Zealand.^f Mercury value is from Witham et al. (2005).^g Thallium value is from Armienta et al. (1998) for Popocatepetl and is a mean of 12 data points.^h Concentrations of H₊ in mol/kg for ashfall and mol/L for water; pH = $-\log [H_+]$. These conversions are necessary because pH scale is logarithmic and values cannot be used directly in model. Calculations are only presented for rainwater tank because buffering capacity in natural waters is likely to make calculations invalid.ⁱ Total hardness = calcium hardness (as CaCO₃) + magnesium hardness (MgCO₃).

may result in waters exceeding the Maximum Acceptable Value of 1.5 mg/L for fluoride in drinking water.

3.4. Domestic rainwater tank

Small, open water supplies are vulnerable to aerial contamination because of their large surface area to volume ratio. It is also important to note that this water is

consumed untreated. Even small amounts of volcanic ash are sufficient to make rainwater-fed supplies undrinkable. For instance, with 1 mm ashfall, the predicted pH value of 5.3 is well outside the range recommended in the Drinking Water Standards for New Zealand of pH 7.0–8.5. Lower-pH water is likely to be plumbosolvent (corrosive towards water tanks and pipes), which will impart a metallic taste and colour to the drinking water,

although this tendency may be offset to some extent by high levels of hardness. At 1 mm ashfall, concentrations of aluminium, iron and manganese are also predicted to be well in excess of aesthetic guideline values (Table 2), particularly for aluminium which exceeds the GV by a factor of 25. At these concentrations of Al, Fe and Mn, water can be expected to have a strong metallic taste and distinct black, brown or red colour. Therefore, while this water may be safe in the sense that no health standards are breached, it is very unlikely to be palatable.

At higher levels of ashfall, concentrations of the potentially toxic elements fluoride, nickel, selenium and thallium exceed primary standards. In these situations, roof-fed tank water is unsafe for drinking as well as being highly unpalatable.

3.5. Upper Mangatawhiri reservoir, Auckland

Considering only a dry weather A/V value of 0.13, the model predicts that even with a 5 mm ashfall, there will be no exceedences of drinking water guideline values for elements of health significance. The only aesthetic determinand predicted to exceed guideline values for drinking water acceptability is aluminium. Even at 5 mm ashfall, exceedences are minor and effects likely to be barely discernible. These findings provisionally suggest that typical eruptions of Mt Ruapehu are unlikely to affect Auckland's drinking water supplies with respect to soluble components of volcanic ashfall. Predicted concentration increases are, for most soluble elements, so small relative to guideline values that even if a proportion of the solutes from ashfall deposited on the entire catchment are assumed to reach the reservoir, few further exceedences of guideline values are predicted.

However, eruptions from volcanic centres closer to Auckland may result in larger quantities of ashfall. We have not attempted to apply the model calculations to this scenario because of the lack of data available on ashfall leachate composition for other New Zealand volcanoes.

3.6. Validation

There is generally a lack of data available for comparison with model predictions, as most measurements made in receiving waters following volcanic ashfall have reported only turbidity and acidity (Table 1), although some studies have paid attention to fluoride contamination (Cronin and Sharp, 2002) and levels of other components such as sulphate and iron (Smithsonian Institution, 2000).

The 1969 eruption of Ruapehu deposited 6–7 mm ash over the western flanks of the mountain, contaminating

water supplies at Iwikau Village (Collins, 1978). Using model input parameters of mean Ruapehu C_{ash} of 86 mg/kg fluoride in ash, a thickness of 6 mm, and the A/V value of 13.0 for a model water tank gives a predicted concentration increase of 6.7 mg/L fluoride, which compares well to the reported value of 6.0 mg/L fluoride measured in a roof water tank (Collins, 1978).

The 2003 eruption of Lopevi volcano, Vanuatu (Cronin et al., 2003b) provides further examples. Two locations were studied:

- (a) Liro, with 1 mm ashfall (density c. 1.5 kg/L), $C_{\text{ash}}=50$ mg/kg fluoride, two tanks with A/V values of 12 and 20 have predicted concentration increases of 0.9 and 1.5 mg/L respectively, comparing well to measured increases of 0.9 and 2.0 g/L (Cronin, unpublished data).
- (b) Luli, with 3 mm ashfall, density c. 1.5 kg/L, $C_{\text{ash}}=65$ mg/kg fluoride, a tank with $A/V=20$ has a predicted increase of 5.9 mg/L, comparing reasonably well to a measured increase of 9 mg/L.

While predicted increases in fluoride concentrations compare well overall to predicted increases in these examples, we acknowledge that the input parameters span a limited range, and therefore that these examples do not constitute a validation of a linear model.

3.7. Limitations of model

The model assumes that, for volcanic ash of a given composition and density, a simple linear relationship will exist between the mass of ash contaminating a water body, and concentration increases of leachable elements. The assumption of linearity may be valid for small quantities of ash but may not apply for larger quantities of ash because saturation limits for minerals of low solubility may be approached or exceeded. Development of a more sophisticated model would need to address this issue.

A further assumption is that elements which are soluble in volcanic ash leachates will remain soluble in receiving waters. In reality, this may not occur because the conditions in natural waters (such as pH, oxidation state and temperature) which control speciation (i.e. the distribution of different chemical forms of each element) are markedly different to those occurring in the surface coatings of volcanic ash, which are known to be highly acidic due to the interaction of volcanic ash in eruption plumes with aerosols such as hydrochloric and sulphuric acids. Strongly acid conditions enhance the solubility of many chemical species, because protons (H^+ ions) swamp

adsorption sites. Thus, elements which are highly solubilised in volcanic ash leachates may be considerably less soluble in natural waters.

For example, the soluble free ion Al^{3+} is dominant under acid conditions ($\text{pH} < 5$), whereas in the range $\text{pH} 5\text{--}9$, which includes most natural waters, insoluble aluminium hydroxide $\text{Al}(\text{OH})_3$ dominates.

For small, open rain-fed supplies such as roof tanks and stock watering troughs, the model should predict concentrations with reasonable accuracy, because rainwater is in itself slightly acidic due to the dissolution of atmospheric carbon dioxide to produce the weakly acidic carbonic acid H_2CO_3 , and has little capacity to buffer against the addition of strong mineral acids such as H_2SO_4 and HCl . However, cement tanks produce slightly alkaline pH values in water, presumably due to the dissolution of carbonate minerals from the concrete (Cronin and Sharp, 2002).

The situation is more complex for natural waters such as lakes or reservoirs, because most natural waters have a pH in the range of $6\text{--}8$ and therefore contain a reservoir of alkalinity (mostly due to the bicarbonate ion HCO_3^-), or buffering capacity against pH change. Although acidification of natural waters after volcanic ashfall has been reported (Table 1), it is unlikely that the addition of a few millimetres of ashfall to a lake or reservoir will, in practice, significantly reduce the pH . Therefore, the model cannot, in general, be expected to predict concentration increases for many components of volcanic ashfall, because their speciation is likely to be different in natural waters compared to volcanic ash leachates. Aqueous geochemical modelling may be a useful tool to predict the behaviour of added ashfall constituents to natural waters.

4. Discussion

Our review of published studies of the impacts of volcanic ash on water supplies suggests that problems associated with high levels of acidity, turbidity and fluoride have been well-documented. However, little attention has been paid to other soluble elements associated with volcanic ash, and their implications for drinking water quality. This is despite the fact that volcanic ash leachates have been well-characterised, with over 55 studies describing their chemical composition (Witham et al., 2005). Our proposed model addresses this information gap.

Applying this model to the effects of Ruapehu ash, from the 1995/1996 eruptions, on two representative water supplies in New Zealand suggests that the contaminants of concern are acidity (pH), Al , Fe and Mn . These contaminants show the greatest tendency to

become elevated to problem levels by ashfall. They are not considered to pose health risks, and therefore are regulated by secondary (non-enforceable) guidelines. However, it is important to note that exceedences of guideline values for Al , Mn , Fe and pH may cause water to become undrinkable due to a bitter metallic taste and dark colour, and may also cause corrosional damage, staining and scale deposition problems in water tanks and pipes. Therefore, the main issues following volcanic ashfall are likely to be shortages of potable water and damage to distribution systems, rather than risks to public health. The application of the model enables these issues to be established on a systematic rather than speculative basis.

For domestic rainwater tanks, the model should work well. The dimensions of individual systems can be accurately determined, and as rainwater generally has a low ionic strength, predicted concentration increases due to soluble elements leaching from ashfall should be close to final concentrations. Furthermore, the model assumes that elements solubilised in volcanic ash leachate will remain soluble in receiving waters. This assumption is probably a reasonable one, as ‘clean’ rainwater is acidic, with a range of $\text{pH} 4.73\text{--}6.01$ reported for a range of remote Southern Hemisphere locations (Halstead et al., 2000) and has low alkalinity. Therefore, chemical conditions in the receiving waters following volcanic ashfall should not be markedly different to those in volcanic ash leachates.

For natural waters such as lakes and reservoirs, there are two important limitations on the utility of this model. The first issue is that the model does not take into account the complexities of speciation in natural waters, particularly with respect to mineral solubilities. The second is that for a water supply reservoir, it is very difficult to predict or measure the extent to which ash from the entire catchment, which usually has a much larger areal extent than the reservoir surface, will contribute soluble elements to the reservoir waters. The first complication may be addressed or overcome by applying aqueous geochemical modelling. Field testing of this model may help address the second complication by relating model predictions to the observed effects of volcanic ashfall on water supply reservoirs.

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