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ABSTRACT

Safe drinking-water, available to everyone, is a fundamental requirement for public health. A safe water supply is also essential for hygiene and sanitation. Volcanic activity can damage or disrupt water supplies in a number of ways. Experience from previous eruptions has shown that in general, for large municipal water treatment systems fed from surface waters such as lakes or reservoirs, the physical impacts of a volcanic ashfall will tend to overwhelm problems caused by chemical contamination resulting from the release of soluble components from the surface of the ash. A particularly important problem is that ash suspended in water increases the turbidity of the raw water supply. Turbidity is a critically important parameter for water treatment, and effective treatment depends on its control. The overall objective of the research described in this report was to investigate a physical (plain settling) and chemical (addition of coagulant) method for removing suspended ash from natural waters. For this work we used a range of natural and synthetic volcanic ash samples with varying characteristics.

The first phase of our investigation was a study of the settling rates through water of different volcanic ashes using plain sedimentation alone. Ash/water suspensions will undergo a rapid initial reduction in turbidity, but there may be a level of residual turbidity that is not amenable to further reductions by plain settling alone. The level of residual turbidity depends on the grain size distribution and surface chemistry of the ash, the initial concentration of ash in water and the chemical composition of the water.

Grain size distribution is a major control on settleability of volcanic ash. Ashes from Ruapehu volcano (1996 eruption) and Pacaya volcano (2010 eruption) were both coarse-grained and had high settleability, with turbidity reducing from initial values of approximately 10-30 NTU at the start of the trial to <5 NTU after 24 hours. In contrast, ash from Chaitén volcano (2008 eruption), which was very fine-grained, settled rapidly initially (from an initial turbidity of 627 NTU reducing to 267 NTU after 30 minutes) but a residual turbidity of 32 NTU remained after 24 hours.

We then assessed the treatability of residual turbidity by the addition of chemical coagulants. Our approach was to use standard jar testing methodology to optimise the dosage of alum (a chemical coagulant that is widely used in conventional water treatment for turbidity removal) in conjunction with the addition of lime ($Ca(OH)_2$) to adjust the pH . It was found that the lowest dose of alum trialled (5 mg/L alum:25 mg/L lime) was effective at reducing the turbidity of a 10 g/L suspension of Chaitén ash to 1 NTU from the initial level of 627 NTU, while not reducing the pH excessively.

KEYWORDS

1.0   INTRODUCTION

Volcanic eruptions can produce a wide range of hazards. Although proximal phenomena such as pyroclastic flows and surges, lahars and ballistics are the most destructive and dangerous, volcanic ash is by far the most widely distributed eruption product (Wilson et al., 2011). Even small eruptions, such as the 1995/96 eruptions of Mt Ruapehu, can cause widespread disruption, damage and economic losses from ashfall impacts on critical infrastructure and primary production (Johnston et al., 2000). Critical infrastructure is defined here as assets that are essential for the functioning of a society and economy. In a broad sense it includes (Platt, 1991):

- Electricity generation, transmission and distribution;
- Gas and oil production, transport and distribution;
- Telecommunication networks;
- Water supply and reticulation (drinking water, waste water/sewage disposal, stormwater and drainage networks);
- Food production;
- Heating (e.g. natural gas, fuel oil)
- Transportation systems (road and rail networks, airports and airspace, ports, inland shipping).

Safe drinking-water, available to everyone, is a fundamental requirement for public health (MOH, 2005). A safe water supply is also essential for hygiene and sanitation. Water is also used for irrigation, livestock drinking water, industrial uses and fire fighting. There are three main ways in which volcanic activity can affect water supplies: 1) by physically destroying or disrupting water sources and components of water supply, treatment and distribution systems; 2) the deposition of volcanic ash into surface waters can change their physical and chemical characteristics; and 3) following an ashfall, there are commonly heavy demands placed on water resources for cleanup purposes and shortages can result if this situation is not properly managed (Stewart et al., 2009a).

Experience from previous eruptions such as the 1980 Mt St Helens (Washington, USA), 1992 Mt Spurr (Alaska, USA), 2008 Chaitén (Chile) and 2010 Pacaya (Guatemala) has shown that in general, for large municipal water treatment systems fed from surface waters such as lakes or reservoirs, the physical impacts of a volcanic ashfall will overwhelm problems caused by chemical contamination resulting from the release of soluble components from the surface of the ash (Wilson et al., 2011; Stewart et al., 2009a, 2009b). Airborne ash can cause problems for water supply equipment such as air-cooled motors, pumps and HVAC (heating, venting and air-conditioning) systems, and there may also be indirect impacts such as electricity outages cutting power supplies to pumps.

A particularly important problem is that ash suspended in water increases the turbidity in open raw water supplies such as rivers and lakes, reservoirs and impoundment basins. In reference to the 1980 eruption of Mt St Helens volcano in the northwestern USA, Hindin (1981) stated that "the immediate and most obvious effect of the ash on surface water supplies was an increase in the settleable solids and turbidity of the water." Turbidity is a critically important parameter for water treatment as:

- Disease causing micro-organisms can adsorb onto or become occluded into suspended particulate matter. This can shield them from the action of disinfectants which are usually added at the end of the treatment train. Therefore it is important to reduce turbidity to as low a level as possible before final (terminal) disinfection or it may not be effective;

- Because it is not practical at present to directly monitor protozoan contaminants such as *Cryptosporidium* and *Giardia*, the removal of turbidity throughout the treatment process is used as a surrogate for the removal of protozoa. Increases in turbidity are perceived as deterioration in the performance of filters with the potential for breakthrough of protozoa.

- Turbidity affects the appearance of the water and makes it less acceptable to the public (MOH, 2005; MOH 2008).

After the 1980 eruption of Mt St Helens, increases in the occurrence of waterborne *Giardiasis* were reported for months afterwards, as far away as the state of Montana. These events were linked to heavy rainfall washing the deposited ash into water supplies (Weniger et al., 1983).

The New Zealand Drinking-Water Standards (MOH, 2008) specify that finished water (i.e. that which is supplied to the consumer) should not exceed 2.5 NTU (nephelometric turbidity units). This is a guideline (i.e. not legally enforceable) value only, as it relates to the aesthetic qualities of drinking water which are considered subjective, and aesthetic parameters are defined as those which affect the potability of the water rather than being public health risks (MOH, 2005). For effective terminal disinfection, the median turbidity must be <1 NTU, with no single sample to exceed 5 NTU. For protozoal compliance, turbidity requirements are more complex and depend on the nature of the water treatment process and the size of population served (MOH, 2005). As an example, for treatment involving coagulation, sedimentation and filtration, with continuous turbidity monitoring, the water leaving each filter must not exceed 0.3 NTU for more than 5% of the compliance monitoring period, must not exceed 0.5 NTU for more than 1% of the period, and must not exceed 1.0 NTU for the duration of any three minute period.

In New Zealand source waters for drinking water supplies, rivers typically have a turbidity of 1-4 NTU but this can increase markedly to >50 NTU or higher during flood flows (MOH, 2005). In the Auckland region, the company Watercare provides drinking water to approximately 1.2 million people. Water sources include 10 storage dams in the Waitakere and Hunua ranges, an intake on the Waikato River, and an aquifer. The dams are in forested catchments and are considered of high quality with turbidity in the range 2-5 NTU. The Waikato River is subjected to geothermal inputs and agricultural runoff, and has a turbidity of 20-40 NTU. However, the Waikato Water Treatment Plant (WTP) has an advanced treatment system and achieves very good turbidity reduction. From Watercare's most recent annual water quality report (2010), the mean turbidity at the Waikato WTP is 0.0145 NTU, compared to mean turbidity levels at the other five treatment plants in the region that range from 0.0224 NTU at the Waitakere WTP to 0.0452 NTU at the Huia WTP. Thus, high turbidity levels in raw water sources do not necessarily lead to problems throughout the treatment process (Watercare, 2010). However, turbidity increases in raw waters can create problems for WTPs that may have less effective treatment processes.

In the event of an ashfall it may be advisable, if alternative water sources are available, to shut down intakes so as to avoid problems caused by suspended ash. Unlike other suspended materials such as silt or clay particles that are normally responsible for turbidity in surface waters, volcanic ash is frequently highly abrasive and can damage pumps and motors as well as clogging intake structures and blocking pipes. Following the 1992 eruption of Mt Spurr volcano, Alaska, turbidity levels in raw water at the Ship Creek treatment facility (one of the two main water sources for the city of Anchorage) increased from normal levels of 0.5-0.6 NTU to 45 NTU the morning after the eruption. The AWWU (Anchorage Water and

Wastewater Utility) was able to close down the intake to protect the facility from excessive turbidity on a precautionary basis, as the company had access to backup raw water sources consisting of 17 deep groundwater wells (Johnston, 1997; Stewart et al., 2009).

However, many water treatment facilities do not have this level of resilience, and thus, there may be significant benefits in investigating the ability of treatment processes to rapidly and effectively remove suspended ash particles from water.

The overall objective of the research described in this report was to investigate simple physical and chemical methods for removing suspended ash from natural waters. For this work we tested a range of natural volcanic ash samples, and a synthetic 'pseudo ash' created in the laboratory. This report describes the preliminary phase of our investigations. In our approach we were guided by an early study by Hindin (1981) which examined treatment options for surface water supplies contaminated by volcanic ashfall from the May 18 1980 eruption of Mt St Helens volcano. This study established that plain (gravitational only) sedimentation, followed by a coagulation-flocculation treatment, successfully reduced the turbidity of ash suspensions. Hindin (1981) remains the only published work on this topic that we are aware of. In the current study, we aimed to build on the findings of this previous work and in particular to investigate the settling behaviour of, and treatment options for, a wider range of volcanic ashes.

2.0   METHODS

Experimental work was carried out in the Environmental Engineering laboratory of the Department of Civil and Natural Resources Engineering, in the University of Canterbury. The method used was a modification of the standard jar test used in water treatment (MOH, 2005) which is a method for determining the optimum parameters for treating a given water source. The common procedure is to initially find the best performing coagulant and dose rate then to determine the optimum pH. Performance is judged on turbidity reduction.

2.1   Coagulation

Coagulation is typically carried out directly on the raw water entering a WTP, with or without a pre-treatment step such as coarse screening to remove large solids. The process of coagulation involves the addition of treatment chemicals to raw water which causes particles to destabilise and aggregate into larger particles which then settle by gravity (MOH, 2005).

The terms 'coagulation' and 'flocculation' are sometimes considered synonymous (for example, by the standard-setting organisation IUPAC). However, the Draft Guidelines for Drinking Water Quality Management in New Zealand (MOH, 2005) define the terms separately and these uses will be adopted in this report. According to these guidelines, coagulants are those chemicals that assist the destabilisation of particles, particularly colloidal sizes, and flocculants are chemicals that assist in the enmeshing of the particles together to form a floc (MOH, 2005).

Most New Zealand water treatment plants use aluminium-based coagulants such as alum (aluminium sulphate, $Al_2(SO4)_3.16H_2O$) or PACl (polyaluminium chloride). A very small number of plants use iron-based coagulants (ferric chloride or ferric sulphate). The most commonly-used flocculants in New Zealand WTPs are polyacrylamide-based polyelectrolytes.

Alum dissociates in water, forming ions which are hydrated. A subsequent series of hydrolysis reactions leads to the liberation of hydrogen ions and, in the appropriate pH range (ph 6-8), the formation of aluminium hydroxide, $Al(OH)_3$, an amorphous floc that settles through the water column. To form flocs, alum requires the presence of alkalinity (eq. 1):

$$Al(H_2O)_6^{3+} + 3HCO_3^- \rightarrow Al(OH)_3\ (s) + 3CO_2 + 6H_2O \qquad \text{(eq. 1)}$$
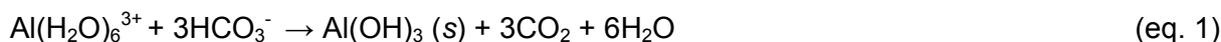
There are two mechanisms by which this process aids floc formation. Firstly, positively-charged species (the original hydrated aluminium ion, plus a range of positively-charged aluminium hydroxide dimers such as $Al_2(H_2O)_4(OH)_2^{4+}$ plus trimers and polymers) act to overcome the repulsive forces between colloidal particles by neutralising the electrical double layer. Many colloids will, in general, flocculate in an electrolyte (Andrews et al., 1996). Secondly, aluminium hydroxide $Al(OH)_3$ is a gelatinous solid that physically carries suspended material with it as it settles.

Ferric chloride ($FeCl_3$), when added to water, also forms a hydrated metal ion with an acidic character analogous to the reaction described above for alum.

Lime ($Ca(OH)_2$), is added to increase alkalinity. This both increases the ionic strength of the water, which aids coagulation by the process described above, and replaces alkalinity consumed by the addition of alum.

2.2   Background on ash settling

'Type I settling' refers to gravitational settling of discrete particles without any interactions with neighbouring particles. Spherical particles will settle at a rate dictated by Stokes's Law (equation 2):

$$v_s = \frac{2}{9} \frac{(\rho_p - \rho_f)}{\mu} g\,R^2 \qquad \text{(eq. 2)}$$

where:

v_s is the particle's settling velocity in m/s (vertically downwards if the density of the particle is greater than the density of water);

ρ_p is the mass density of the particle in kg/m^3;

ρ_f is the mass density of the fluid in kg/m^3;

μ is the dynamic viscosity in Ns/m^2;

g is the gravitational acceleration in m/s^2; and

R is the radius of a spherical object in metres.

The grain size of a volcanic ash deposit depends primarily on the distance from the source and the strength of the source eruption (Pyle, 1989). Generally, ash particles in distal deposits range in size from several hundred to a few microns in diameter. The settling velocities (following Stokes's Law behaviour) of these particles in water vary from approximately 5 cm/s for the larger particles in this size range through to 0.014 cm/s (~0.5 m/hr) for a 15 μm diameter particle, implying that long residence times are possible in deep water bodies (Carey, 1997).

However, volcanic ash particles frequently have highly irregular, non-spherical shapes (Mele et al., 2011), and thus their settling behaviour is not expected to be predicted accurately by Stokes's Law (Ferguson et al., 2004; Wilson and Huang, 1979). Further considerations include influences of lateral currents and vertical gravity currents (e.g. Cashman and Fiske, 1991; Carey, 1997). The latter arise when a flux of airfall tephra arrives at the water surface, and slows in velocity as it crosses the air/water interface, leading to an increased concentration of particles in the boundary layer. Initially a dilute front of particles moves downwards but if the concentration of the particles in the boundary layer continues to increase to the point where it becomes convectively unstable and generates descending plumes, this has the overall effect of accelerating particle settling.

Few studies have investigated the settling behaviour of very fine ash. Rose and Durant (2009) note that the very fine ash component of distal airfall deposits has been a neglected area of study because generally, distal deposits form an ephemeral, irregular covering over a large area which may be quickly reworked and further dispersed by wind and rain, and therefore present considerable difficulties for sampling. These authors reconstructed total grain size distributions for several recent explosive eruptions and concluded that basaltic eruptions have small proportions (~1-4%) of very fine ash (defined as being <30 μm) whereas silicic eruptions typically contain 30-50%. Horwell (2007) investigated grain size distributions in ash samples obtained for a range of recent and historic eruptions, with the aim of assessing proportions of ash in the health-relevant size fractions <4 μm (respirable) and <10 μm (thoracic). The proportions of ash in these extremely fine fractions increase with increasing explosivity. The May 1980 eruption of Mount St Helens (VEI 5), for example, had 11.74% <4 μm and 24.5% <10 μm by cumulative volume in a sample collected in Spokane, 378 km from the vent (Horwell, 2007).

Extremely fine particles are expected to have very slow rates of settling in water, and thus may lead to persistent turbidity problems. Colloidal particles (those in the size range 1 nm to 1 μm) may be stably suspended in water. For water treatment, the application of coagulant chemicals is likely to be necessary for turbidity reduction.

2.3 Analytical methods

Turbidity was measured with a HACH Model 2100P Portable Turbidimeter which operates on the nephelometric principle. Its operating range is 0.01-1000 NTU and its accuracy is ±2% of readings.

Suspended solids (SS) were measured as per Method 2540-D from the handbook of Standard Methods (APHA , 2005). This method involves vacuum filtering a known volume of the water sample through a pre-weighed Whatman glass fibre filter circle Grade GF/C, 90 mm diameter, that has been previously oven-dried at 103-105°C for at least 24 hours. Suspended solids are calculated from the difference between the final dried weight of the filter paper and its original weight, divided by the sample volume.

A pH electrode and RE357T$_x$ microprocessor pH meter was used to measure pH, while conductivity was measured using a YSI Model 30 handheld conductivity, salinity and temperature system. Its operating range is 0-499.9 μS/cm with an accuracy of 0.5% of readings.

Alkalinity was determined by the standard titration method 2320-B (APHA, 2005). This latter method involves determining the volume of 0.02M H_2SO_4 required to titrate a known volume of sample to an endpoint of pH 4.5.

3.0 VOLCANIC ASH SETTLING TRIALS

3.1 Settling of volcanic ash in different waters

3.1.1 Chaitén ash sample

For the initial phase of this work, a single ash sample ('Chaitén ash') was used. It was selected on the basis that we had quantities sufficient for multiple trials and because of its fine grain size (Figure 2) which implied that it would settle slowly enough to discriminate between the different water composition types trialled. The sample was collected from a 36 cm thick deposit of primary airfall ash by our field team at a distance of approximately 25 km from Chaitén volcano (Chile), in January 2009.

The 2 May 2008 eruption of Chaitén volcano was highly explosive (VEI 4-5; see Newhall and Self, 1982 for definition of VEI) and was composed of high-silica rhyolite (Pallister et al., 2010). Distal ashfall deposits contained high proportions in very fine size fractions. Ashfall collected in Esquel, Argentina (103 km from the vent) on 8 and 10 May 2008 contained approximately 10% (by cumulative volume) <4 μm and ~21% <10 μm (Horwell et al., 2010). Samples collected in the town of Jacobacci, 307 km from the vent, contained similar proportions in these size fractions.

Field water quality measurements obtained during our January/February 2009 field visit to the Chaitén region indicated that turbidity levels, due to the presence of suspended ash, remain high in many surface waters. For example, in Lago Espolón, located approximately 65 km from Chaitén volcano, the turbidity at the time of our visit was 18.2 NTU whereas previously the lake was described by local residents and municipal authorities as being 'crystal clear' (<1 NTU).

The Chaitén ash sample used in this research was collected closer to the vent than the samples described above (Horwell et al., 2010) and thus was expected to be skewed towards coarser size fractions. However, size analysis revealed that it contained sufficient very fine ash to be suitable for these trials (Figure 2).

3.1.2 Settling of Chaitén ash in different waters

The initial phase of this study was to investigate the settling of Chaitén ash in three different waters. The purpose was to choose one water type for use in subsequent flocculation experiments. Rates of settling were expected to be different in waters of different ionic strength (see Section 2.0). The waters trialled were Christchurch tap water, deionised water produced in the laboratory, and a surface water sample from Lake Dunstan, Central Otago. The characteristics of these waters are presented in Table 1.

Table 1   Characteristics of waters used in initial settling trial of Chaitén ash

	Deionised water[1]		Reservoir water[2]		Tap water[3]	
	Mean	S.D.	Mean	S.D.	Mean	S.D.
Alkalinity (mg/L CaCO$_3$)	5.0	0.4	38	3	53	5
pH	6.6	0.1	6.30	-	7.4	0.1
Conductivity (μs/cm)	5.4	1.9	96	6	142	6
Turbidity (NTU)	1	0.1	40	2	1	0.1

[1] Four measurements, samples collected on 5/5/2011 and 13/5/2011
[2] Three measurements, one sample collected 5/5/2011
[3] Based on 8 measurements for samples collected on 5/5/2011, 13/5/2011, 18/5/2011 and 31/5/2011

Settling trials were carried out using Chaitén ash at an initial concentration of 10 g/L. Hindin (1981) used suspensions of 1 g/L and 50 g/L of Mt St Helens volcanic ash for treatability studies; the value of 10 g/L is intermediate in this range. For a straight-sided container, the concentration of suspended ash depends only on the thickness of ashfall and the water depth and is given by the following formula: ash concentration (g/L) = ashfall thickness (in mm)/water depth (m). Typical water reservoirs are several metres deep; for instance, the ten reservoirs that are the basis of Auckland's water supply range in depth from 4-10 m at minimum storage volume and 6-19 m at maximum storage volume (Johnston et al., 2004). Thus, ashfall thicknesses of 40-100 mm and 60-190 mm (for minimum and maximum storage respectively) are required to produce concentrations of 10g/L of ash in water in these reservoirs. These can be regarded as credible ashfall thicknesses from a proximal eruption source such as an Auckland Volcanic Field eruption, dependent on wind direction and strength and eruption magnitude and explosivity (Molloy et al., 2009). Such thicknesses are far less probable from a distal eruptive source, although the 1314 AD Kaharoa eruption from Tarawera volcano deposited ~2 cm of ash on eastern Auckland (200 km away) (Nairn, 2002).

Volcanic ash can also be washed into lakes and reservoirs from catchments, and windy conditions can re-suspend ash. Overall, the concentration of 10 g/L was chosen to be at the high end of expected scenarios following an eruption to provide a good test for treatment methods.

Ash was mixed (using a paddle stirrer) with each water type to form a suspension using a mixing period of 1 min at 100 rpm. The paddle stirrer was removed and samples were then left to settle. Water quality parameters (conductivity, turbidity and pH) were measured by removing sample aliquots from approximately 1 cm below the surface of each sample jar. The parameters were measured at times of t=0, 0.5, 1, 1.5, 2,3,4,12,24 and 48 hours. Three separate measurements were made of turbidity at each time interval and one of pH and conductivity. The trial was repeated on three different days (5/5, 11/5 and 13/5).Trends in turbidity measurements over 48 hours are shown in Table 2 and Figure 1. The experiments were carried out at room temperature (approximately 20°C).

Table 2   Changes in turbidity due to settling of 10g/L suspensions of Chaitén ash in different waters

	NTU					
	Deionised water		Reservoir water		Tap water	
Time (hours)	Mean[1]	S.D.	Mean	S.D.	Mean	S.D.
0	1006	103	961	244	881	113
0.5	414	132	403	9	218	152
1	291	112	251	34	144	98
1.5	230	60	194	46	113	78
2	202	72	172	52	89	60
3	135	2	140	30	81	43
4	112	11	113	31	66	37
12	72	28	106	70	45	38
24	30	16	105	-	29	19
48	25	-	50	-	14	-
Turbidity of water alone[2]	1	0.1	40	2	1	0.1

[1] Results presented are averages of analyses carried out on 5/5, 11/5 and 13/5 with three replicates per sample. Reservoir water was analysed only on 5/5 and 11/5.
[2] From Table 1.

For all three water types, there was rapid initial settling, with approximately 90% reduction of turbidity occurring within the first four hours. Between four and 48 hours the reduction in turbidity was much less dramatic. Residual turbidity at the end of the trial ranged from 14 NTU in Christchurch tap water to 50 NTU in Lake Dunstan (reservoir) water.

Mean turbidity levels in the Christchurch tap water suspensions were consistently lower than for the other two water types (Figure 1). This is consistent with the expected ionic strength effect on colloid removal, as the Christchurch municipal tap water supply had the highest conductivity. However, turbidity measurements in these initial studies had a wide range (Table 2) and the apparent difference could be statistically insignificant.

Christchurch tap water was chosen for use in subsequent experiments on the basis of its ready availability and broad similarity in ionic strength to natural surface waters. Water collected from Lake Dunstan was not practical to obtain and use in large amounts, and also had a high background level of turbidity, so was excluded from further trials. To minimise day-to-day variations in the composition of tap water (the Christchurch municipal water supply), a 50 litre tank of this water was collected and stored. The relevant properties of the water (pH, conductivity and alkalinity) were recorded each time trials were conducted and were not found to vary over the duration of the trials.
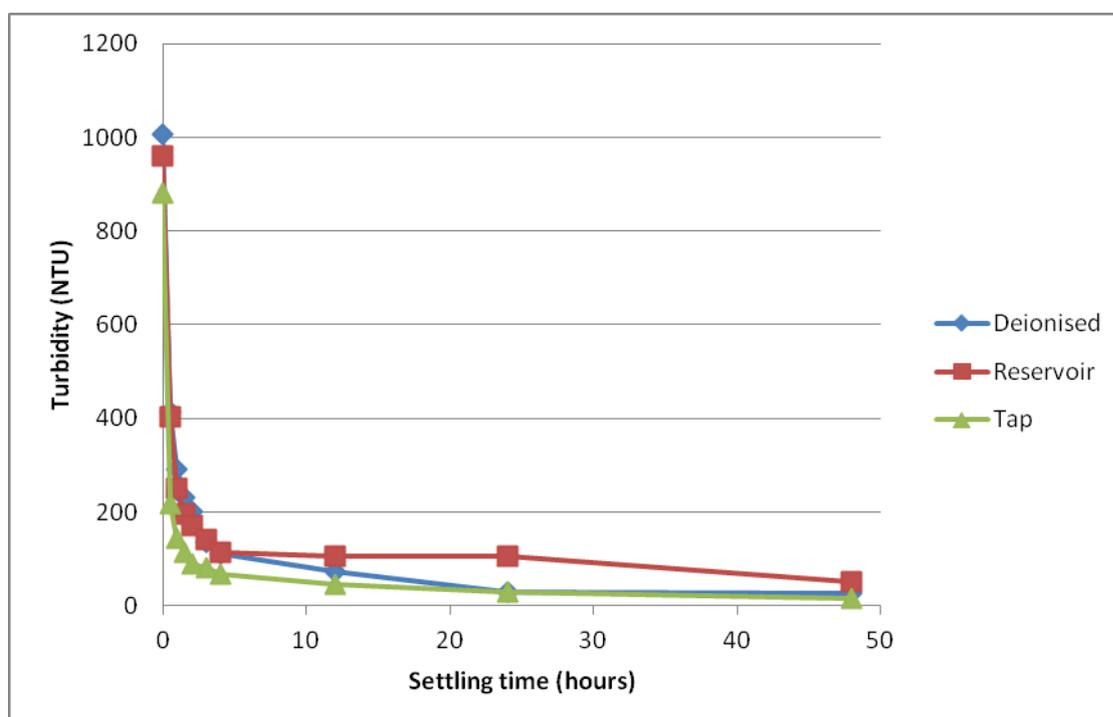
Figure 1   Changes in turbidity due to settling of 10 g/L suspension of Chaitén ash in different waters

3.2   Settling of different volcanic ashes

The trials described in the previous section were repeated with three different volcanic ash samples, in order to establish their settling behaviour. The ash samples used are described in Table 3 and their grain size distributions presented as Figure 2. Grainsize distributions of the ashes were obtained by using a Partica LA-950 laser diffraction particle size analyser. In the case of the Pacaya ash, samples were dry sieved into fractions >1 mm and <1 mm. Each ash was sampled two or three times and underwent a minimum of five analytical runs in the particle size analyser to ensure repeatability of the results. The output values were averaged and then plotted graphically to show the distribution curves (Figure 2). In addition

to these natural ash samples, two samples of synthetic ash created in the laboratory at Canterbury University were used. Basaltic lava from Lyttelton volcano (Stoddard basalt) was crushed and milled to a fine-grained ash. One sample was dosed with a strongly acidic solution (Ruapehu Crater Lake water, see Appendix 1 for composition), giving the dried ash properties similar to fresh volcanic ash, and the other sample was untreated. Full details of methods used to prepare and characterise synthetic ash are given in Broom (2010) and summarised in Appendix 2. The synthetic ashes have been designed as a laboratory proxy that can be mass-produced, and as part of their validation process were included in this study to characterise their performance against the four real ash samples. The ash samples are shown in Figure 3.

Table 3   Characteristics of volcanic ash samples and synthetic ash used in settling trials

| Eruption	Eruption Date	Distance from vent	Composition (wt. % SiO$_2$)	Description	Reference
Pacaya, Guatemala	27 May 2010	13 km	Basalt (49.1%)	Black, well vesiculated, friable, poorly sorted, fine lapilli to coarse ash scoria	Wardman et al. 2011
Ruapehu, New Zealand	17 June 1996	100 km	Andesite (57.8%)	Dark grey - dark brown, poorly sorted, coarse to medium ash	Cronin et al. 2003
Chaitén, Chile	2-6 May 2008	25 km	Rhyolite (72.8%)	Light grey to white, poorly sorted, medium to fine ash.	Watt et al. 2009
Synthetic ash: Stoddard basalt, Lyttelton volcano, New Zealand	5.8 – 7.0 Ma	< 5 km	Basalt (~43%)	Dark grey, olivine and clinopyroxene basalt	Sewell 1988
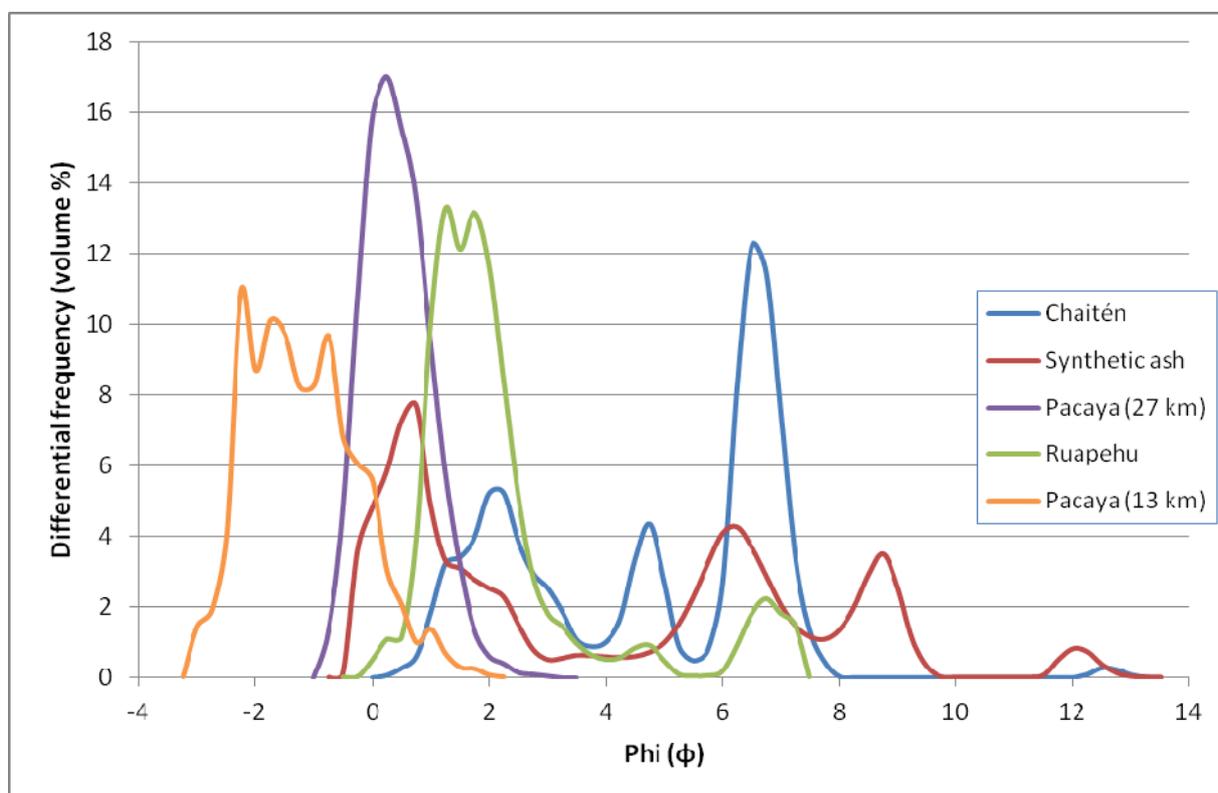
Figure 2   Grain size distributions of ash samples, determined by sieving and laser-diffraction sizing
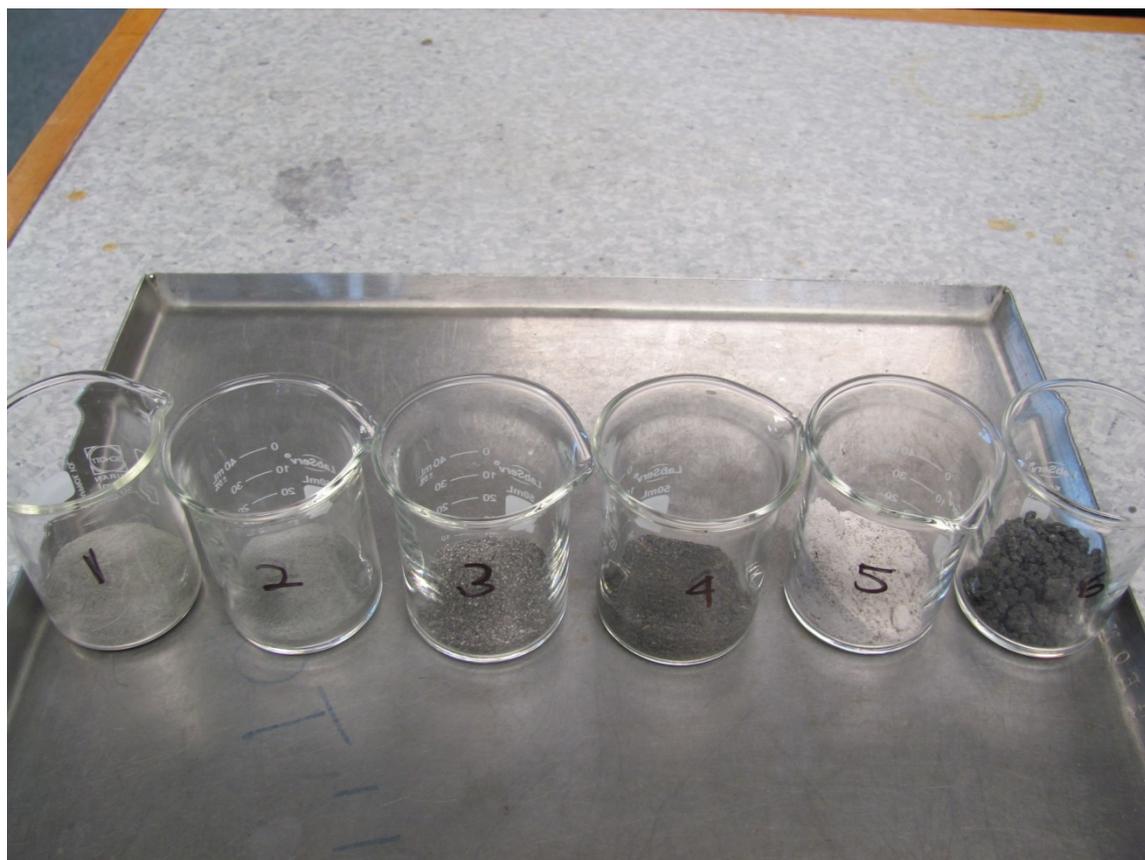
Figure 3   1=dosed synthetic ash, 2=non-dosed synthetic ash, 3=Ruapehu, 4=Pacaya <1 mm, 5=Chaitén, 6=Pacaya >1 mm

Ash suspensions were prepared by mechanically stirring ash with the stored tap water at a concentration of 10 g/L, for one hour at 100 rpm. Results are shown in Table 4 and Figures 4 and 5 (note different scales).

Table 4   Turbidity readings during settling of ash samples (10 g/L suspension in tap water)

Turbidity (NTU)											
	Ruapehu		Pacaya >1 mm		Pacaya <1 mm		Chaitén		Dosed synthetic ash		Non-dosed synthetic ash	
Hours	Mean[1]	s.d.[1]	Mean	s.d.	Mean	s.d.	Mean	s.d.	Mean	s.d.	Mean	s.d.
0	30.9	3.5	9.1	0.5	18.0	1.2	627	84	1924	47	1482	598
0.5	8.8	0.3	7.2	0.2	12.9	0.2	267	60	410	110	823	32.4
1	4.9	0.0	5.5	0.2	11.2	0.3	297	46	270	22.7	775	10.1
1.5	4.8	0.2	5.1	0.0	10.3	0.4	238	3	307	3.1	529	5.0
2	5.9	0.1	5.3	0.2	10.6	0.4	213	7	225	6.4	534	12.5
3	5.4	0.0	5.5	0.3	10.5	0.9	189	2	241	5.0	495	13.6
6	4.5	0.0	4.1	0.1	7.7	0.5	69	1	173	110	185	2.7
12	2.6	0.1	3.4	0.1	6.2	0.1	62	1	73	3.6	163	2.1
24	1.5	0.1	2.3	0.1	4.2	0.2	32	0	31	0.8	82	0.2

[1] All turbidity data is the mean of three individual readings at each time interval.
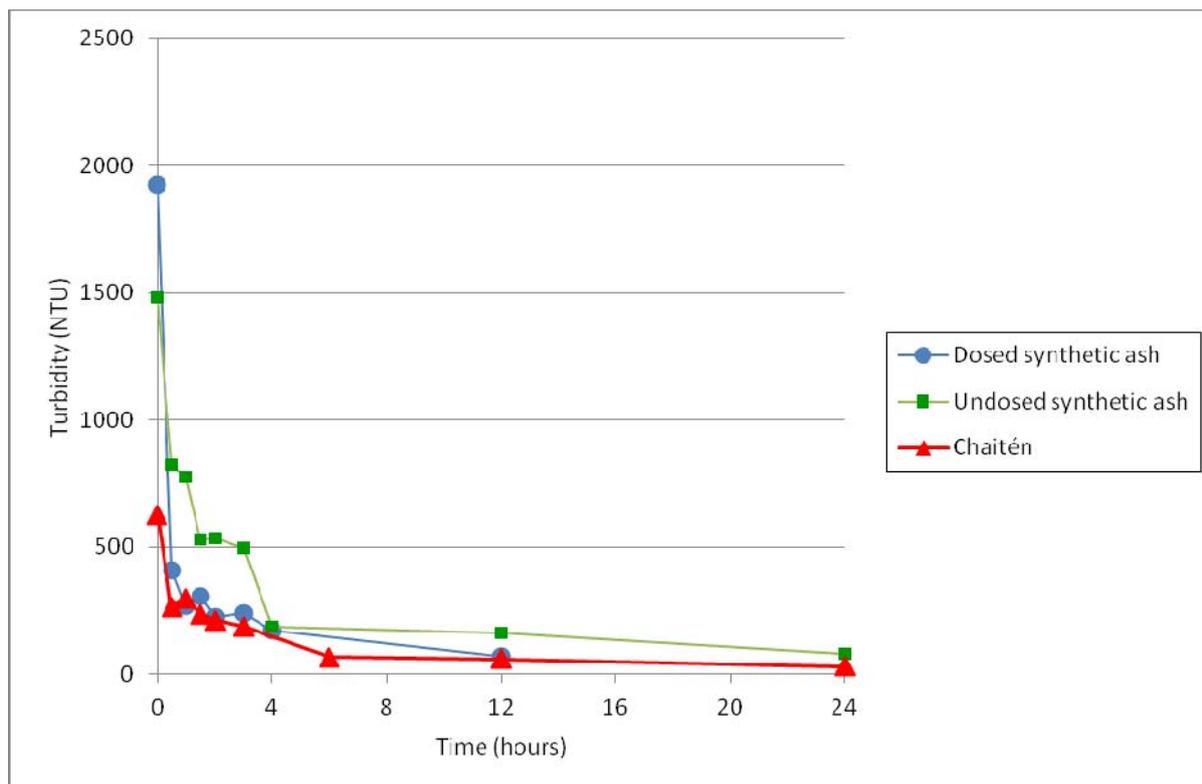
Figure 4   Turbidity reduction during settling trials of 10 g/L suspensions of Chaitén and dosed and non-dosed synthetic ash samples
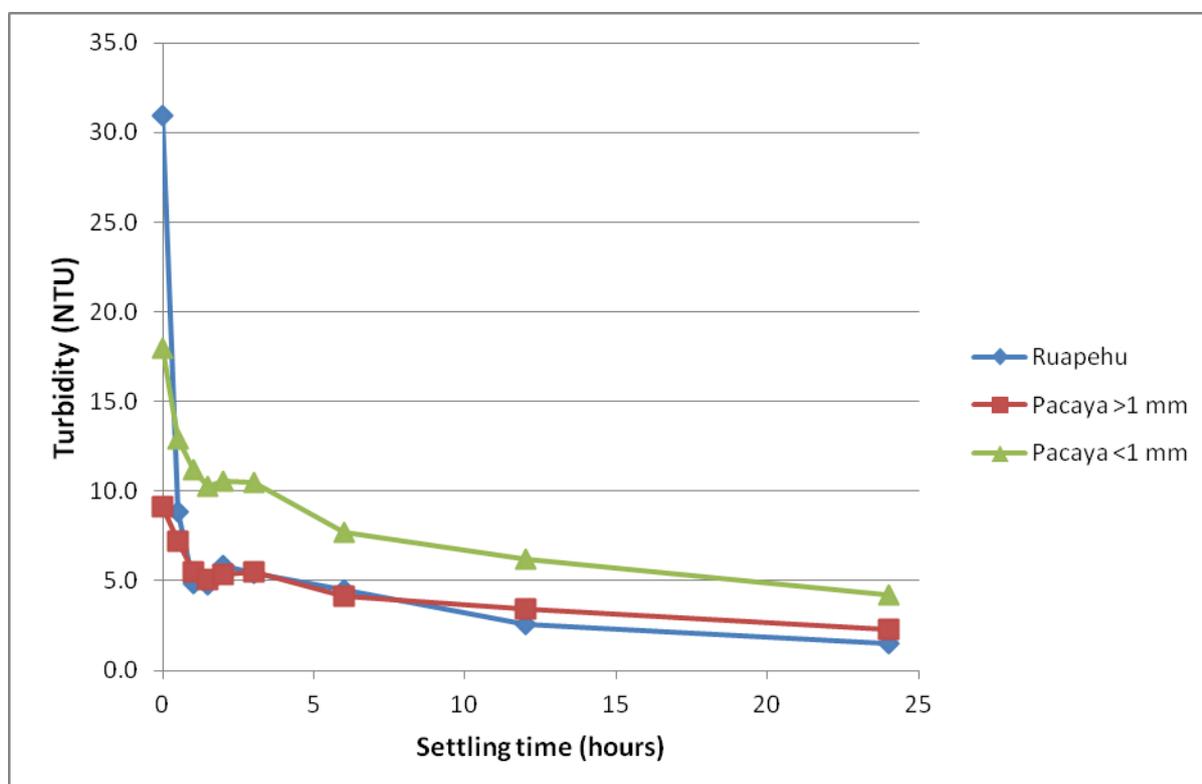
Figure 5   Turbidity reduction during settling trials of 10 g/L suspensions of Ruapehu and Pacaya ash samples
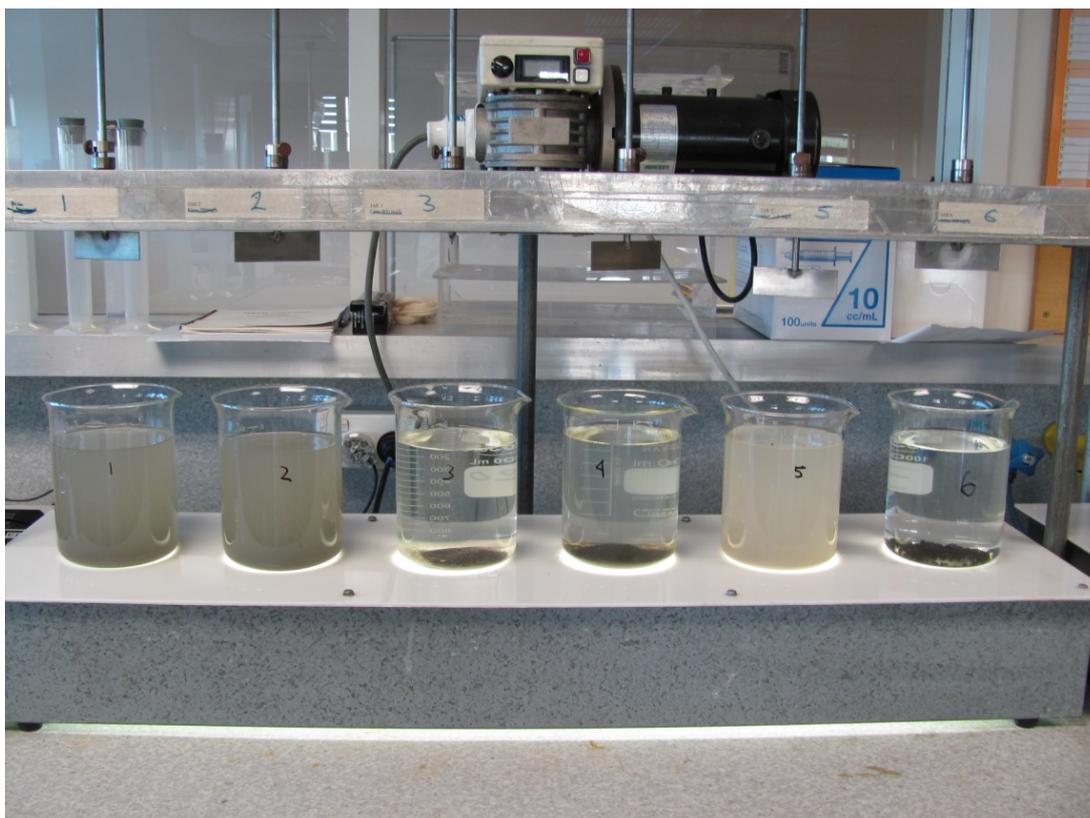
Figure 6   Ash-water suspensions after one hour continuous mixing at 100 rpm followed by one hour settling (see Figure 4 for identity of samples)

All ash samples showed the same general trends in settling behaviour seen in Figure 1, with a high initial settling rate within the first few hours, with relatively little further change after this. There was a clear difference between the Chaitén and synthetic ash samples (both dosed and non-dosed), which had very high initial turbidity, and the Ruapehu and Pacaya ash samples, which had initial turbidity levels almost two orders of magnitude lower. Turbidity levels after 24 hours' settling were correspondingly different between these two groups, with the Chaitén and synthetic ash samples showing residual turbidity levels >30 NTU, and the other ashes having much lower residual turbidity levels of <5 NTU.

3.2.1 Influence of soluble surface salts

The more rapid settling of the dosed compared to non-dosed synthetic ash (Figure 4) is probably due to the increased ionic strength added by the dosing solution, which acts as a coagulant aid (Section 2.1). Trends in conductivity data (which indicate gross chemical changes in the suspensions) for the six ash samples over the 24-hour are shown in Figure 7.
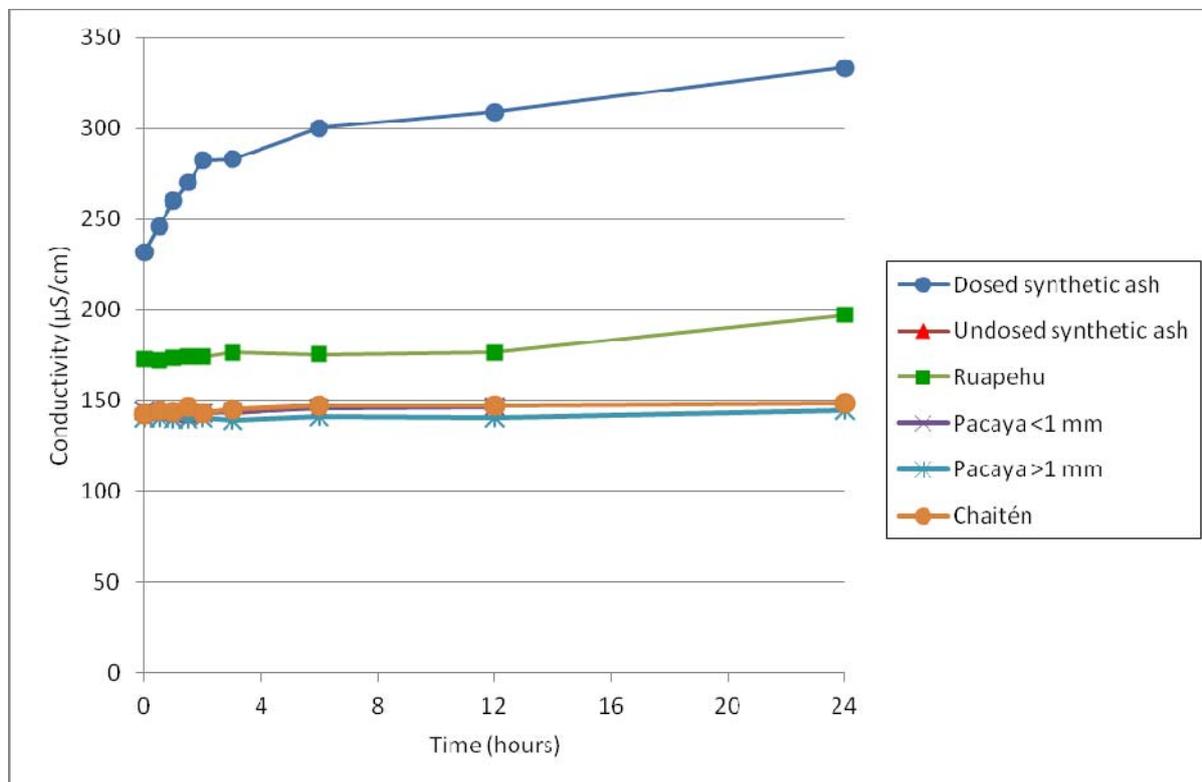
Figure 7   Trends in conductivity during settling trial for different ash samples

Four of the six ash samples (both Pacaya samples, Chaitén and the non-dosed synthetic ash sample) changed the conductivity of the suspension little from the initial value, for tap water, of 145 µS/cm. This indicates that these samples contained few soluble salts on their surface. Both the Chaitén and the Pacaya ash samples were known to have been affected by rainfall prior to collection, which would have washed away their soluble coating. The Ruapehu ash sample was collected within 24 hours of the eruption and has been kept in dry storage, and appears to have retained at least some of its soluble surface salts as it caused an increase in conductivity from the baseline value of 145 µS/cm, to approximately 175 µS/cm. The dosed synthetic ash sample, as expected, released the greatest amount of soluble salts on contact with water, as it gave rise to a conductivity of approximately 280 µS/cm after four hours settling. This continued to increase with longer settling times, indicating the continuing release of soluble salts from this material.

3.2.2 Relationship between ash grain size distribution and settling rates

To investigate the relationship between the grain sizes of the different ash samples trialled and the observed rates of settling, levels of turbidity remaining in solution at settling times of one hour, two hours, 12 hours and 24 hours were plotted against grain size. As the Chaitén, Ruapehu and synthetic ash samples are all polymodal (Figure 2), measures such as mean or median grain size are unlikely to be meaningful. The proportion of each ash sample (by volume) smaller than 4Φ (62.5 µm), 5Φ (31.25 µm) and 6Φ (16 µm) were plotted against turbidity data (Figure 8). It was found that the grain size threshold used did not make much

difference to the ability to discriminate between the different samples, so 5Φ was chosen arbitrarily. This threshold is also defined by Rose and Durant (2009) as being the upper size limit of 'very fine ash'.
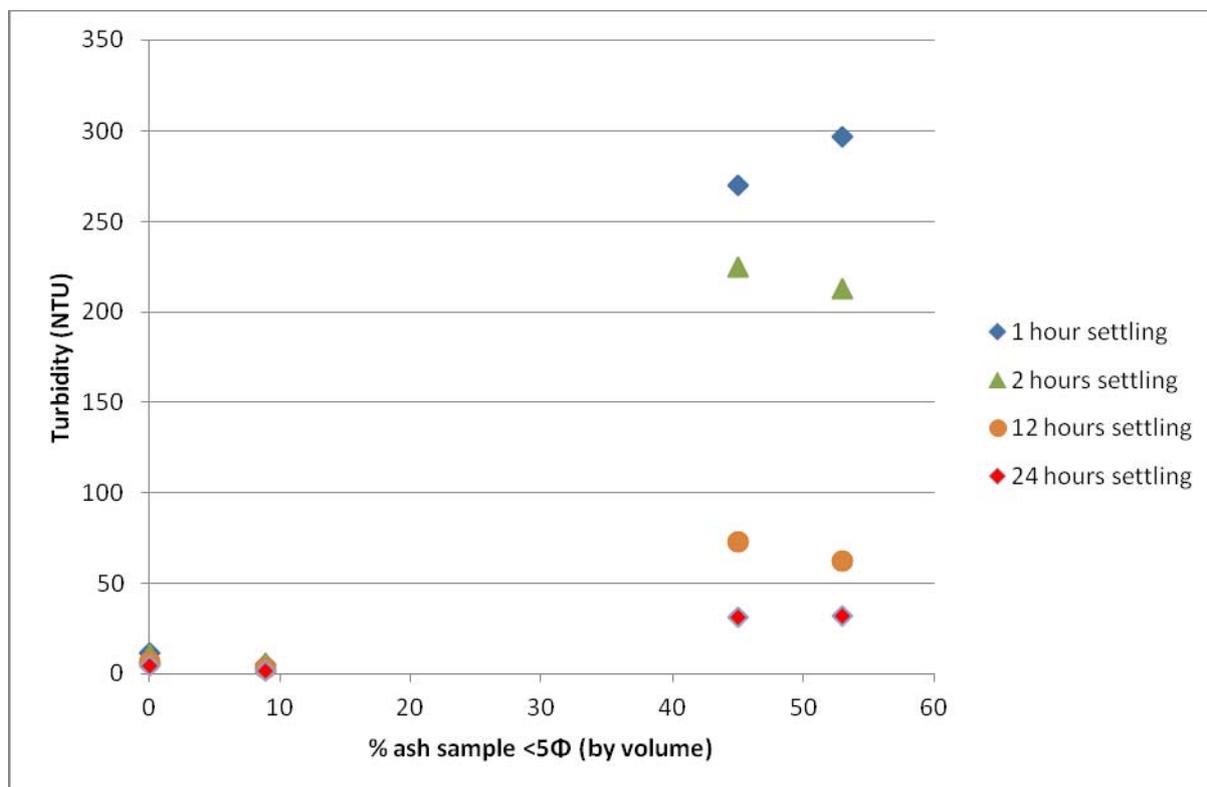

Figure 8   Ash grain size versus turbidity at four different settling times (10 g/L initial concentration of ash)

There is a general relationship between the 'residual turbidity' remaining at each settling time, and the proportion of very fine material in each sample, with the two samples containing finer grain sizes (Chaitén and the synthetic ash) having higher levels of turbidity at all settling times than the two coarser samples (Ruapehu and Pacaya). Considering a linear fit to the data for each settling time, the Ruapehu ash lies below this line of best fit for all settling times, implying that it has settled faster than predicted on the basis of grain size. This may be because it had a relatively high soluble salt content (Figure 7) which could have increased the rate of settling of the tail of fine material (Figure 2) in this sample. The Chaitén ash also settled noticeably faster than expected at the settling times of two hours and 12 hours. This material contained very low levels of soluble salts (Figure 8) so this would not have caused the faster settling of this material. Figure 2 shows that although Chaitén ash has a higher proportion than synthetic ash of material <31 μm, it has less of a tail of extremely fine material <8Φ (4 μm) than the pseudo ash, so that the threshold value chosen (5 Φ) may not be a good predictor of relative settling rates of these two ash samples.

Thus, from this preliminary study, it may be tentatively concluded that ash grain size distribution is in general a good predictor of the rate of settling over a range of time periods, from one hour to 24 hours. The soluble salt content of the ash also appears to be a contributing factor for finer particle sizes.

3.3   Characterisation of leachates for different volcanic ashes

The standard method for characterising the soluble surface coating of volcanic ash is by performing a deionised water leach (Witham et al., 2005; Hagemann, 2007). For the ash

samples described in Table 3, three parameters (pH, conductivity and alkalinity) were recorded for suspensions of ash in deionised water using a range of ash concentrations (5, 10 and 50 g/L). Each suspension was mixed at 100 rpm for one hour, then subsamples were removed after times of 2 hours and 24 hours. Results are shown in Table 5 and Figures 9 and 10.

Table 5   Conductivity, pH and alkalinity for suspensions of ash in deionised water[1]

Time	Measured parameter	Dosed synthetic ash (g/L)			Chaitén (g/L)			Ruapehu (g/L)		
		5	10	50	5	10	50	5	10	50
2hr	pH	5.40	5.63	5.64	6.19	6.00	6.21	4.63	4.45	4.04
	conductivity (µS/cm)	47.3	85.5	354.9	7.6	5.7	16.8	62.7	94.3	336.0
	alkalinity (mg/L CaCO$_3$)	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0	0
24hr	pH	5.92	5.90	5.77	5.44	5.86	5.81	4.62	4.51	4.19
	conductivity (µS/cm)	51.3	90.7	376.2	11.3	12.2	18.4	64.0	100.3	351.2
	alkalinity (mg/L CaCO$_3$)	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0	0

[1] Initial conductivity of deionised water 5.4 µS/cm (Table 1)

Alkalinity in the leachates was close to the detection limit of the method and will not be discussed further here. As seen in Table 5, the Chaitén ash leachate had the lowest conductivity, indicating that soluble salts that might have been present at the time of ashfall, have largely been leached from this material. Ruapehu and dosed synthetic ash leachates had similar levels of conductivity across the concentration range, and at both two and 24 hours of contact time (Figure 9). An approximately linear relationship between ash concentration and conductivity was seen indicating that saturation effects are not significant at these ratios of ash to water. In their comprehensive review of ash-leachate methods, Witham et al. (2005) reported that at a high ash:water ratio of 1:4, complete dissolution of some minerals such as gypsum was hindered due to supersaturation of the solution with respect to these minerals. This was not generally a problem at lower ash:water ratios, and Witham et al. (2005) recommended a ratio of 1:25 as a generally applicable standard method for characterising ash leachates. The ratios used in this study ranged from 1:20 to 1:200, thus the observed linear relationship between ash concentrations and conductivity is expected.

Extending contact time from 2 to 24 hours made little difference to conductivity, confirming that release of soluble salts is rapid in deionised water. Hindin (1981) reported similar observations for Mt St Helens ash. Witham et al. (2005) recommended an agitation time of 90 minutes based on reviewing several studies that indicated that the majority of adsorbed surface salts dissolved within an hour.

The Ruapehu ash was found to generate the most acidic leachate. Jones and Gislason (2008) noted that the pH of fresh ash leachates is highly variable, and is thought to depend primarily on the presence of an acidic gas condensate. Ash from the 2000 eruption of Hekla was found to be the most acidic, with an initial pH of 3.5 on contact with deionised water. Neutral to basic ash leachates have also been reported. For example, Gislason et al. (2011) reported that the pH of ash leachate from the explosive phase of the April 2010 Eyjafjallajökull eruption was slightly basic at pH 8; this was thought to suggest the absence of an acidic gas condensate as volatiles were removed in the glacial meltwaters in this early, hydromagmatic phase.

For the ash samples tested in this study, the pH of the Ruapehu ash was lower at higher ratios of ash:water, indicating the presence of an acidic gas condensate on this material. The

Chaitén ash leachates were less acidic than Ruapehu ash leachates (Cronin et al. 2003). This material is thought to have lost its soluble surface salts. The observed pH is not dramatically different from the initial pH of deionised water (approximately pH 5.7) and probably reflects the initial dissolution of volcanic glass. It should be noted that Ruggieri et al. (2011) reported that fresh Chaitén ash caused the pH of deionised water to increase to weakly alkaline (pH 8.04). This was attributed to the interaction between multioxide silicate mineral phases and water consuming protons (Oelkers, 2001).

The dosed synthetic ash leachates had similar pH values to the Chaitén ash leachates. This is perhaps surprising as these samples were dosed with strongly acidic solutions, thus might be expected to have readily-soluble acidic surface salts which should produce acidic leachates. It is possible that the added protons have completely exchanged with cations in the silicate lattice of the mineral phase; this is consistent with Delmelle's proposal that the range of observed sulphate and halide salts found on fresh volcanic ash are formed by rapid acid dissolution of ash particles within eruption plumes, which is thought to supply the cations involved in the deposition of sulphate and halide salts (Delmelle et al., 2007). In support of this contention, Oelkers (2001) reported that selective leaching of metals from silicate lattices is coupled to proton consumption, consistent with metal-proton exchange reactions.
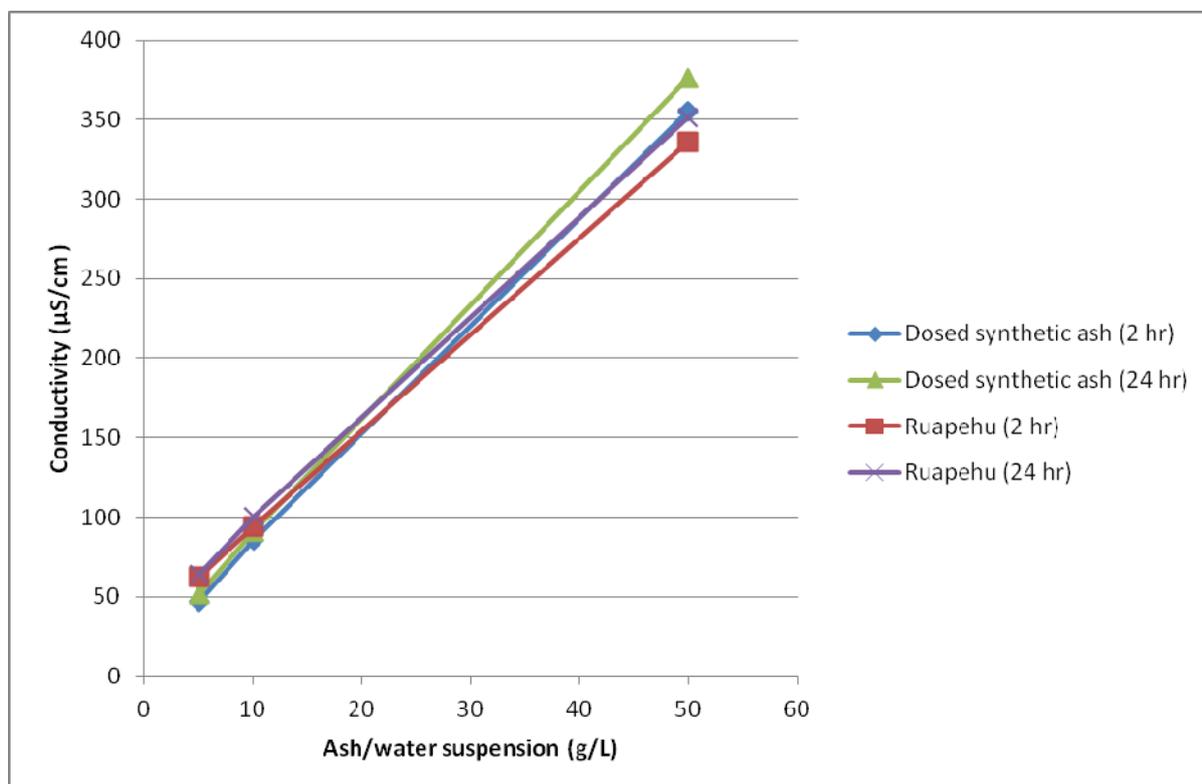
Figure 9   Conductivity of ash/water suspensions
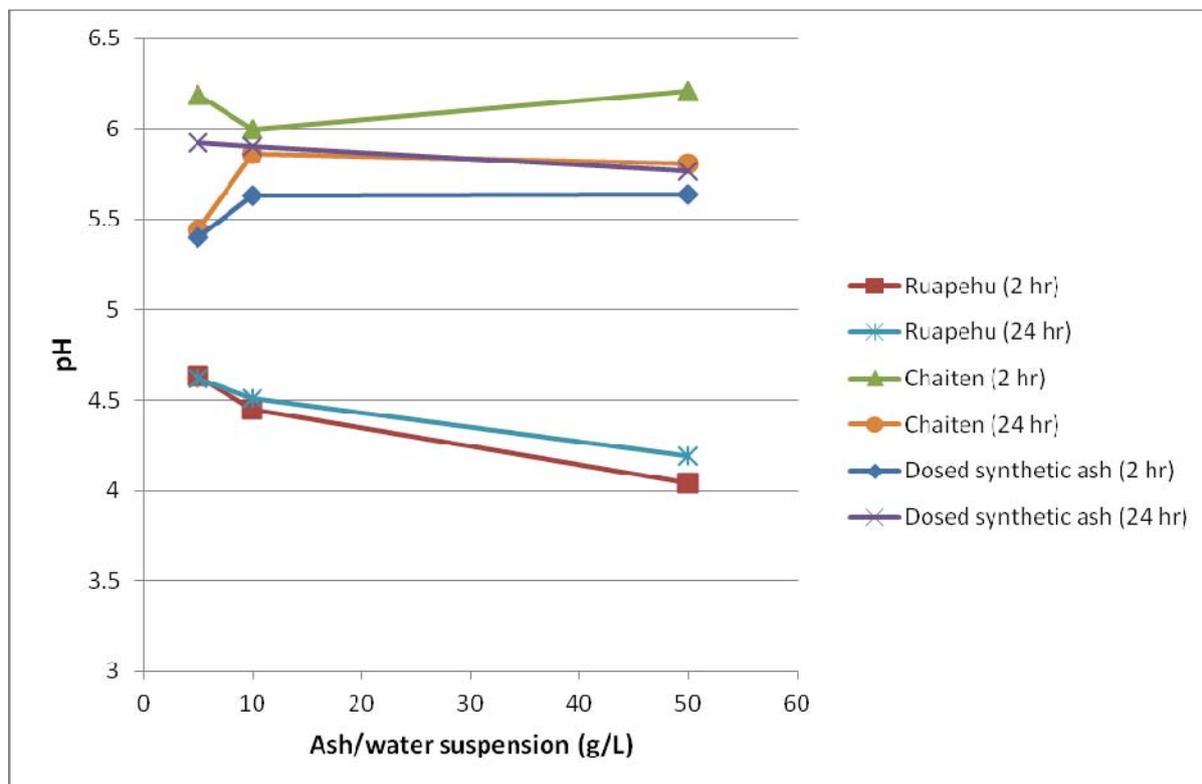
Figure 10   pH of ash/water suspensions

3.4   Conclusions from initial trials

The results presented here demonstrate that different volcanic ashes settle at different rates, with grain size distribution being a major control. For two of the coarser-grained, mafic (low silica) ash samples trialled (Ruapehu and Pacaya), settling rates are rapid and turbidity is reduced to levels of less than 5 NTU within a few hours. This implies that for ashfall events of similar grain size, settling alone may be sufficient to decrease turbidity to a level where it is unlikely to be problematic for water treatment facilities, as background turbidity levels in water supplies are typically approximately 5 NTU (Section 1).

However, in the event of a very fine ashfall (such as the Chaitén ash), settling alone is unlikely to reduce turbidity to levels acceptable in raw water supplies, as these ashes contain significant proportions of very fine material, and even after extended settling periods, residual turbidity levels are still high (>30 NTU). In these cases the application of coagulation/flocculation treatment is likely to be advantageous.

The next section of this report outlines the development of a treatment process for volcanic ash using chemical coagulants.

4.0 COAGULATION/FLOCCULATION TRIALS TO ENHANCE SETTLING

The purpose of this part of the study was to investigate the treatability of aqueous ash/water suspensions using standard coagulation-flocculation agents. As a starting point we referred to Hindin (1981) who found that alum ($Al_2 (SO_4)_3 \cdot 16H_2O$) was an effective treatment for removing colloidal ash particles from Mount St Helens volcanic ash suspensions, but that its effectiveness was dependent on pH, alkalinity, the ash concentration and the settling time. In these trials, the standard jar test (described in Section 2) was used to determine optimal dosages of treatment chemicals.

4.1 Methods

Samples of natural and synthetic ash and stored tap water (10 g/L) were mixed with a Phipps and Bird paddle stirrer at 100 rpm for one hour. Samples were then left to settle for an hour (to take advantage of the high initial rate of settling occurring during this time), then the supernatant was decanted and used in coagulation/flocculation trials. The Pacaya ash samples were not included in these trials as it was previously found that settling alone was effective in reducing turbidity to acceptable levels.

Varying doses of alum and then alum plus lime ($Ca(OH)_2$), were added to the supernatant, and mixed for one minute at 100 rpm and then 20 minutes at 25 rpm. The solutions were then allowed to settle for a one hour period, then the supernatants decanted and tested for turbidity, suspended solids (in mg/L), conductivity, pH and alkalinity. Suspended solids were determined by filtration and weighing, and the other parameters by the methods described previously in Section 2.3. Duplicate samples were run to determine reproducibility.

4.2 Treatment using alum

An initial set of trials were run using alum only as a coagulant. The doses used were 0, 2, 6, 10, 14 and 18 mg/L alum (as Al) with the 0 mg/L corresponding to the 'control alum dose'. Results are shown in Table 6. Turbidity reduction data is summarised in Table 7 for the alum dose that produced the highest reduction in turbidity.

For both the Chaitén and synthetic ash samples, dosing with alum resulted in enhanced turbidity reduction compared to the reduction expected if settling alone had occurred for 24 hours. However, this turbidity reduction was accompanied by an approximately twofold increase in conductivity, a reduction in pH to a level of pH 4.4 in all cases, and a reduction in alkalinity. These changes are consistent with the known mechanism of action of alum as a flocculant (Section 2.0) whereby its hydrolysis consumes alkalinity and generates acidity. Such low pH levels are likely to require further treatment with lime in a water treatment process; thus the next stage of these trials was to determine the optimal ratio of alum:lime.

Table 6   Coagulation/flocculation trials using alum only, on 10g/L ash:water suspensions

Alum dose (mg/L as Al)	Turbidity (NTU)			Mean	s.d.	Conductivity (µS/cm)	pH	Alkalinity (mg/L as CaCO3)	Suspended Solids (mg/L)
Dosed synthetic ash replicate 1									
0	203.1	181.5	208.8	198	14	213	6.8	75	151.0
2	41.1	42.3	40.8	41	1	224.5	6.73	25	40.0
6	101.1	98.7	101.7	101	2	262.1	5.17	5	102.6
10	73.8	67.8	67.8	70	4	294.5	4.67	5	77.2
14	42.3	39.3	42.6	41	2	389	4.44	0	44.6
18	24	21	21.6	22	2	442.6	4.36	0	17.6
Dosed synthetic ash replicate 2									
0	203.1	181.5	208.8	198	14	213	6.8	75	151.0
2	22.2	24.6	25.5	24	2	226.0	6.03	30.0	25.2
6	101.7	96.0	93.6	97	4	257.2	5.12	5.0	108.8
10	78.9	76.2	78.0	78	1	293.9	4.69	5.0	88.4
14	37.5	38.1	39.0	38	1	393.8	4.44	0.0	42.8
18	10.5	9.3	9.9	10	1	445.6	4.37	0.0	0.0
Chaitén									
0	146.1	155.7	154.5	152	5	143.9	6.85	40	225.8
2	52.5	51.0	51.6	52	1	153.8	6.66	30	100.0
6	101.7	102.6	106.2	104	2	189.7	5.17	5	204.2
10	109.5	101.1	97.8	103	6	226.7	4.75	0	179.8
14	52.8	52.8	52.5	53	0.2	321.7	4.51	0	92.2
18	11.7	12.0	12.3	12	0.3	390.8	4.44	0	14.4
Ruapehu									
0	3.5	3.9	3.0	3.5	0.5	182.5	6.07	10	2.4
2	5.5	5.9	5.6	5.7	0.2	190.1	5.88	5	14.0
6	8.4	7.0	8.2	7.9	0.8	255.2	4.80	5	19.4
10	7.6	7.8	7.8	7.7	0.1	290.7	4.65	0	15.4
14	8.0	7.7	7.8	7.8	0.2	377.8	4.49	0	10.2
18	2.8	2.4	2.5	2.6	0.2	441.7	4.39	0	4.2

Table 7   Turbidity removal data: alum dosing compared to plain settling (10 g/L suspensions)

Ash	Turbidity (NTU)				
	Initial turbidity[1]	After 1 hr settling[1]	After 24 hr settling[1]	Control alum dose[2]	Alum dose (18 mg/L as Al)[2]
Ruapehu	31	4.9	1.5	3.5	2.6
Chaitén	627	297	32	152	12
Dosed synthetic ash	1924	270	31	198	16[3]

[1] From Table 4
[2] From Table 6
[3] Mean of two replicates, see Table 6 for raw data

4.3 Treatment using combined lime/alum dose

Combined alum/lime doses were trialled to determine the optimal dose for turbidity reduction from 10 g/L ash/water suspensions of the dosed pseudo ash and Chaitén ash. Results are presented in Table 8. Changes in turbidity and pH for dosed synthetic ash are shown in Figures 11 and 12, and for the Chaitén ash in Figures 13 and 14. A summary table of turbidity and suspended solids removal is shown as Table 9.

Table 8   Coagulation/flocculation trials using combined alum/lime dosing, on 10g/L ash/water suspensions

| Alum dose (mg/L Al)	Lime dose (mg/L Ca(OH)$_2$	Turbidity (NTU)			Mean	s.d.	Conductivity (µS/cm)	pH	Alkalinity (mg/L CaCO$_3$)	Suspended solids (mg/L)
Dosed synthetic ash, alum:lime 1:5										
0	0	231	246	237	238.0	7.5	250.9	7.26	60	175.6
5	25	3	3	3	3.0	0.0	337.0	6.50	55	4.6
10	50	1	2	1	1.3	0.6	351.6	5.67	30	3.0
25	125	2	2	2	2.0	0.0	656.0	4.20	0	2.2
50	250	2	2	2	2.0	0.0	897.0	4.22	0	0.6
100	500	10	10	11	10.3	0.6	1081.0	8.87	70	14.8
Dosed synthetic ash, alum:lime 1:6										
0	0	231	246	237	238.0	7.5	250.9	7.26	60	175.6
5	30	2	2	2	2.0	0.0	297.8	7.08	55	1.2
10	60	1	1	1	1.0	0.0	373.3	6.57	35	0.6
25	150	2	1	1	1.3	0.6	672.0	4.47	0	2.6
50	300	3	3	3	3.0	0.0	940.0	4.53	0	4.2
100	600	1	1	1	1.0	0.0	1135.0	9.53	175	2.6
Chaitén ash, alum:lime 1:4										
0	0	123	129	129	127.0	3.5	183.0	7.0	50	132.0
5	20	2	2	2	2.0	0.0	223.0	6.1	15	3.6
10	40	1	2	1	1.3	0.6	287.2	4.8	0	2.4
25	100	2	1	1	1.3	0.6	516.0	4.4	0	2.0
50	200	3	3	3	3.0	0.0	1012.0	4.0	0	6.4
100	400	5	6	6	5.7	0.6	1230.0	5.9	25	8.0
Chaitén ash, alum:lime 1:5										
0	0	123	129	129	127.0	3.5	183.0	7.0	50	132.0
5	25	1	1	1	1.0	0.0	255.7	6.1	30	1.2
10	50	1	2	1	1.3	0.6	312.4	5.8	10	0.2
25	125	2	2	2	2.0	0.0	525.0	4.8	0	1.4
50	250	2	2	2	2.0	0.0	838.0	4.6	0	2.4
100	500	43.1	39.6	38.0	40.3	2.6	1376.0	5.3	70	73.4
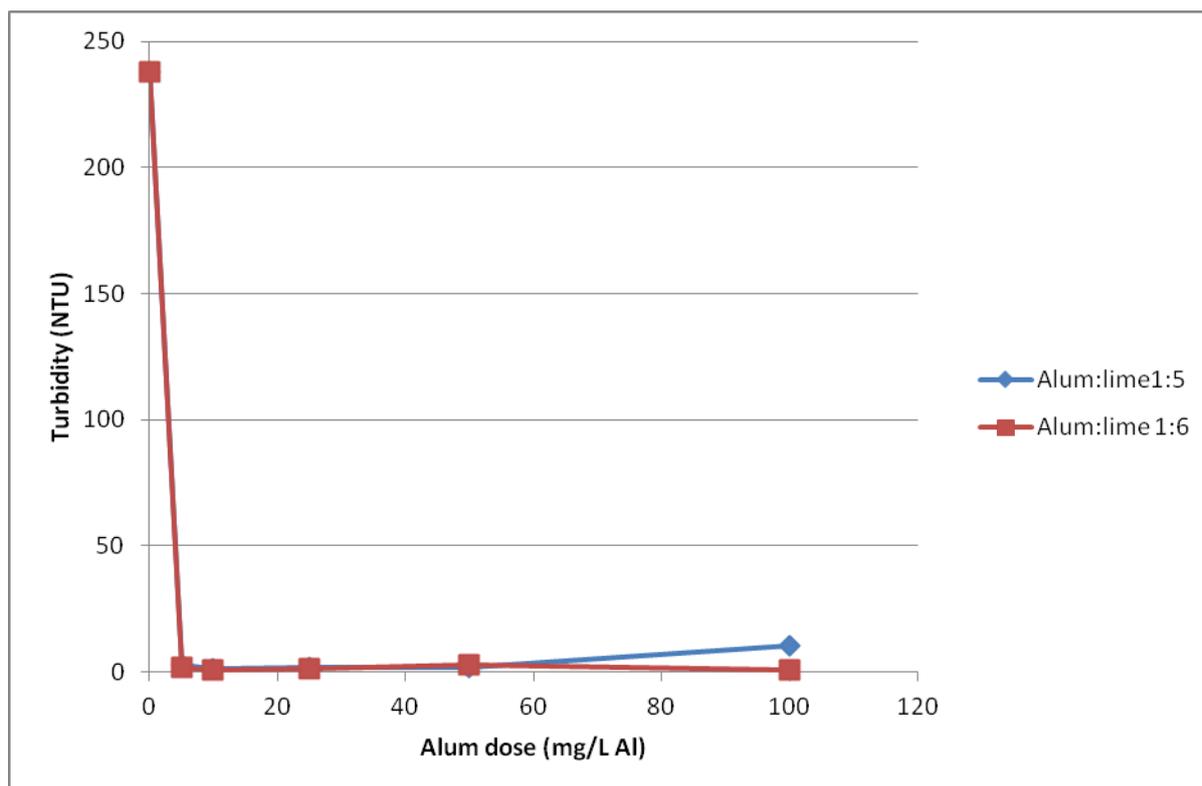
Figure 11   Changes in turbidity with increasing alum dose, dosed synthetic ash
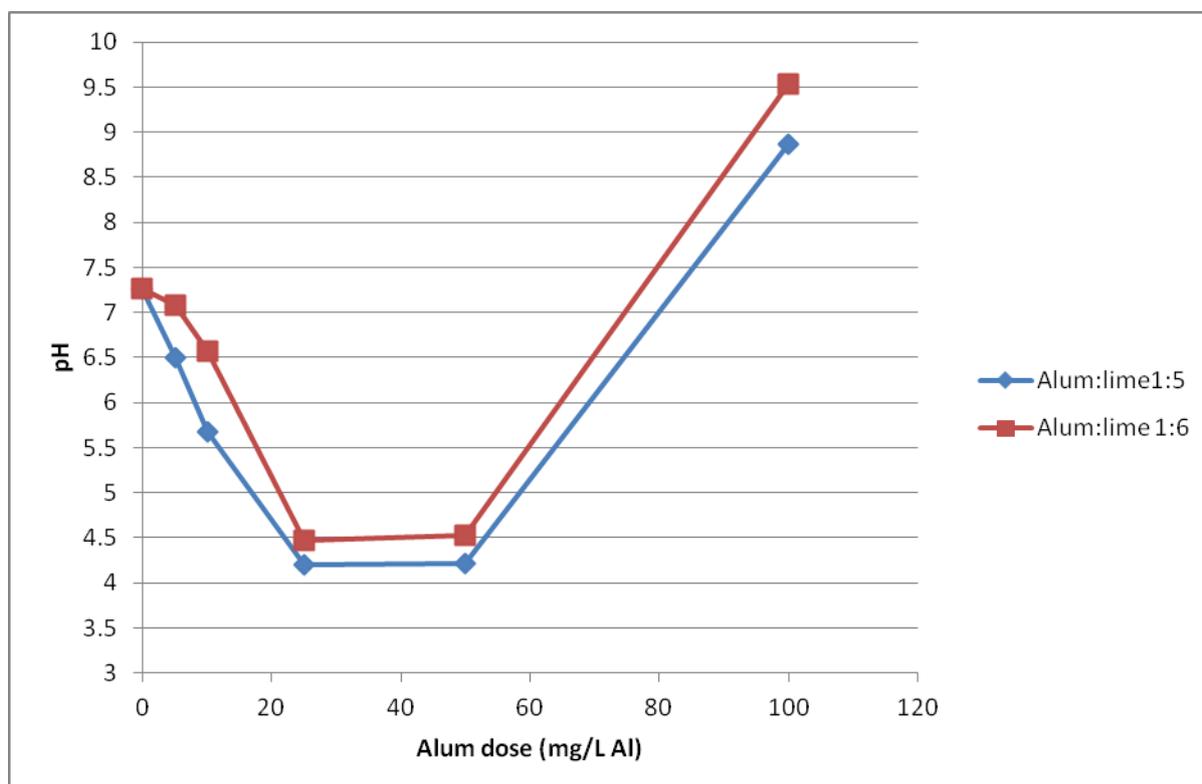

Figure 12   Changes in pH with increasing alum dose, dosed synthetic ash
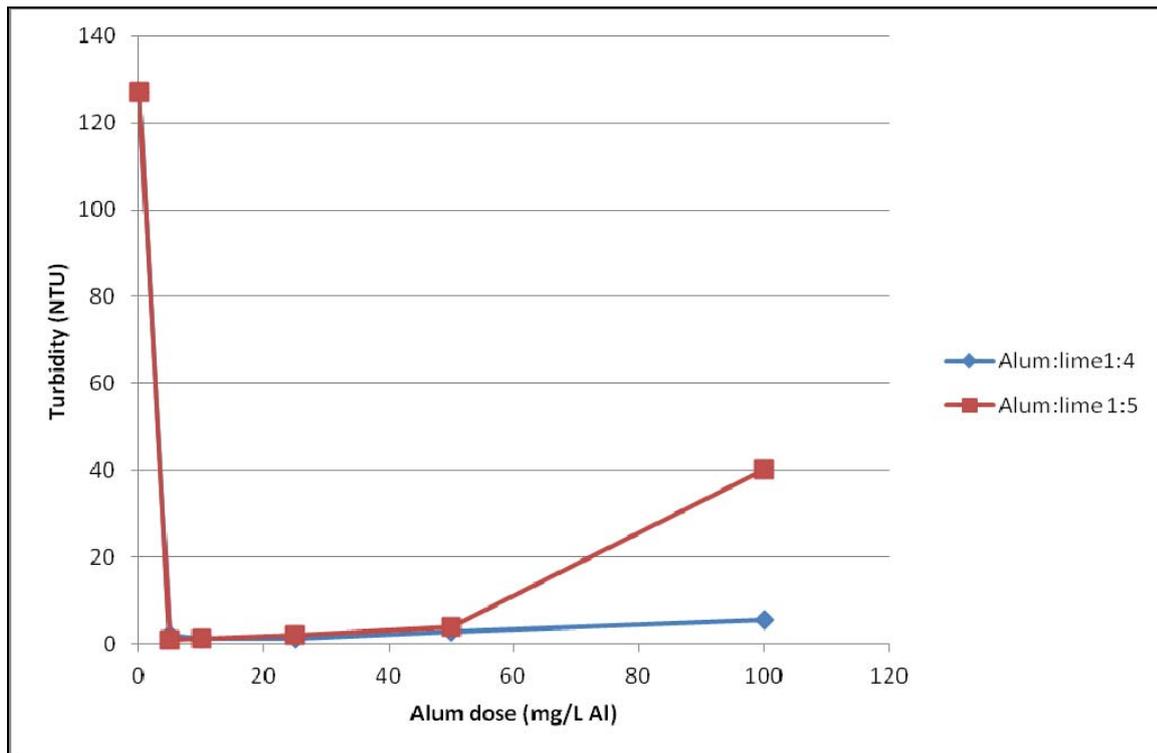
Figure 13   Changes in turbidity with increasing alum dose, Chaitén ash
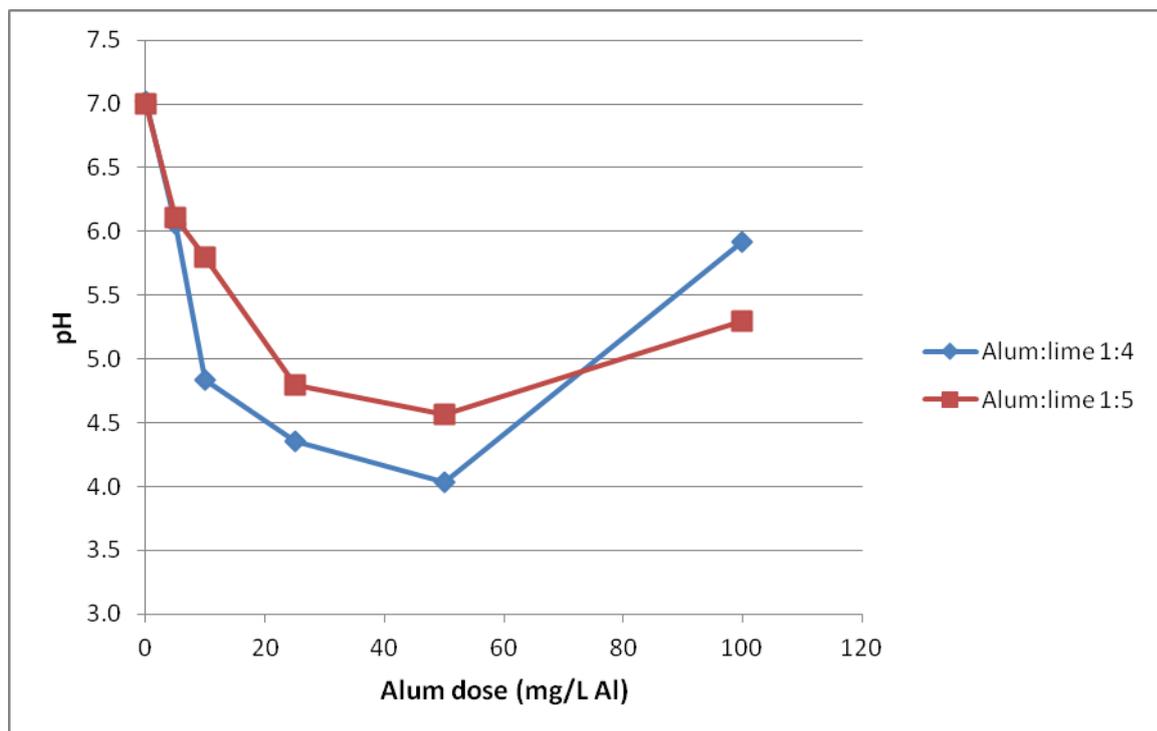

Figure 14   Changes in pH with increasing alum dose, Chaitén ash

Table 8   Turbidity removal data: combined lime/alum dosing compared to plain settling (10 g/L suspensions)

Ash	Turbidity (NTU)				
	Initial turbidity[1]	After 1 hr settling[1]	After 24 hr settling[1]	Control alum/lime dose[2]	Optimal alum:lime dose[3]
Chaitén	627	297	32	127	1
Dosed synthetic ash	1924	270	31	238	1

[1] From Table 4
[2] From Table 9
[3] For Chaitén ash, optimal dose was 1:5 alum (5 mg/L):lime (25 mg/L); for dosed pseudo ash the optimal dose was 1:6 alum (10 mg/L): lime (60 mg/L).

All doses trialled resulted in major turbidity reductions; however, as the alum dose increased, the pH decreased to unacceptably low levels (Figure 11) as was observed for alum-only dosing (Table 6). The use of a higher proportion of lime was partially successful in offsetting the pH decrease, for concentrations up to 50 mg/L Al.

Overall, considering both turbidity removal and the avoidance of unacceptably large pH changes, the best results were obtained at some of the lowest combined alum/lime doses trialled. For the dosed synthetic ash, alum doses of 5 and 10 mg/L (as Al) accompanied by the addition of lime at a 1:6 ratio of alum:lime were both successful at achieving turbidity reductions to 1-2 NTU while not excessively lowering the pH . For the Chaitén ash, the same doses of alum accompanied by the addition of lime (1:5 ratio) also achieved very good turbidity reduction but the pH drop observed suggested that increasing the proportion of lime is necessary.

5.0   SUMMARY AND CONCLUSIONS

5.1   Comparisons with Hindin (1981) study

The aim of this study was to build on the findings of an investigation by Hindin (1981) on treatment options for volcanic ash from the 1980 eruption of Mt St Helens volcano. In particular we wished to include a wider range of volcanic ash samples of different characteristics. The Hindin study was based on a volcanic ash sample collected at Pullman, Washington, 388 km from Mt St Helens. The characteristics of Mt St Helens ash collected at various locations were thoroughly described by Fruchter et al. (1980). The ashfall at Pullman was fine-grained, with approximately 80% (by weight) in the size range 20-45 μm (approximately 4.5-5.5 Φ), and just 5% <20 μm (>5.5 Φ). From comparison with Figure 2 it can be seen that the Chaitén ash sample used in this study contains a greater proportion of finer-grained material than the Mt St Helens sample, but that the Pacaya and Ruapehu samples are coarser. Thus a reasonable range of grain sizes has been included in this study.

Hindin found that while plain settling reduced turbidity rapidly in ash:water suspensions, the reduction was only partial. For a 1 g/L suspension of ash in water, reduction of turbidity from an initial value of 110 NTU to approximately 50 NTU occurred within the first 40 minutes, but after that, no further reduction in turbidity was observed. The same pattern was also observed for a 200 g/L suspension. This led to a conclusion that plain sedimentation is a simple and rapid method for reducing the turbidity of ash-contaminated water, particularly at higher ash concentrations (>10 g/L). It is important to bear in mind that the conclusions reached by Hindin are valid only for the ash sample trialled and should not be generalised to all volcanic ashes.

The current study built on Hindin's approach of characterising both the settleability and treatability of volcanic ash, but extended the work to assess a wider range of volcanic ash samples (with a wider range of grain sizes). Settling trials were also carried out for more extended periods of time, for greater applicability to real situations (ashfall deposition into standing water bodies). For all samples, there were major reductions in turbidity within the first one to two hours of the settling trials (Figures 4 and 5). For the coarser samples such as Pacaya >1 mm, the initial turbidity at the start of the trial is very low (9.1 NTU), probably because rapid settling occurred prior to the first measurements being made, thus further turbidity reductions are slight rather than dramatic.

Overall, the results obtained in this study reinforce Hindin's findings that ash/water suspensions will undergo a rapid initial reduction in turbidity but that there may be a level of residual turbidity that is not amenable to further reductions by plain settling. The level of residual turbidity appears to be dependent on the grain size distribution of the ash, the initial concentration of ash in water, the surface chemistry of the ash and the chemical composition of the water.

The treatability of residual turbidity by the addition of chemical coagulants was carried out both by Hindin and in the current study. In both cases the approach was to use standard jar testing methodology to optimise the dosage of alum (a chemical coagulant that is widely used in conventional water treatment for turbidity removal) in conjunction with the addition of lime ($Ca(OH)_2$) to adjust the pH . Hindin found that the alum dose necessary to reduce turbidity is dependent on the initial concentration of ash and on the alkalinity. In the current study, only one initial ash concentration (10 g/L) was investigated due to time constraints. It was found that the lowest dose trialled (5 mg/L), in conjunction with the addition of lime, was the most effective at both reducing turbidity to 1 NTU while maintaining the pH in an acceptable range.

5.2   Applicability to water treatment

The results of this study suggest that in the event of ash deposition into an open standing water source, such as a lake or reservoir, rapid settling will occur in the first few hours that will substantially reduce the turbidity from its initial level. Depending on the characteristics of the ashfall (grain size distribution, surface chemistry), the thickness of the ashfall and the composition of the surface waters, there may be residual turbidity in the water column that is not amenable to further reduction by plain settling alone. Settling trials conducted on a range of different volcanic ash samples suggested that grain size distribution is a major control on settleability. Ashes from Ruapehu volcano (1996 eruption) and Pacaya volcano (2010 eruption) were both coarse-grained and appeared to have high settleability, with turbidity reducing from initial values of approximately 10-30 NTU at the start of the trial to <5 NTU after 24 hours. In contrast, ash from Chaitén volcano (2008 eruption), which was very fine-grained, settled rapidly initially (from an initial turbidity of 627 NTU reducing to 267 NTU after half an hour) but a residual turbidity of 32 NTU remained after 24 hours. Similar trends were reported (Hindin, 1981) for the fine-grained ash that fell at a distance of 388 km from Mt St Helens volcano (1980 eruption); a 1 g/L suspension underwent a rapid reduction in turbidity from an initial level of 110 NTU to approximately 50 NTU in just 40 minutes, but no further turbidity reduction was seen.

It is important to note that these trials were carried out under laboratory conditions, and care must be taken in projecting the findings more generally. Standing water bodies such as reservoirs and dams will be subjected to processes such as wave action that can resuspend deposited material. A further difference is that in these trials ash was mixed directly into the water to form a suspension whereas volcanic ash will be deposited aerially, in which case particle settling can be more rapid if convectively-unstable vertical gravity currents form (see Section 2.2).

In the event of an ashfall leading to higher levels of turbidity that persist beyond a few hours in duration and are not amenable to further reduction by settling alone, options for treatment will depend upon the capacity of the treatment plant in question to manage turbidity in raw water. If the turbidity is within the range of raw water turbidity normally encountered by the WTP due to flood flows, it will be unlikely to cause difficulties for the plant and will be subjected to the normal initial coagulation/flocculation step in the treatment train. Levels beyond the normal operating range may prompt considerations such as temporarily closing intakes to allow for further settling, or adjusting the initial coagulation/flocculation treatment step.

An additional factor to consider is that unlike most material (such as clay particles) that is usually responsible for turbidity, volcanic ash is typically highly abrasive and can cause severe damage to pumps and motors. It is therefore worth considering measures to limit its ingress into water treatment plants, independently of its effects on turbidity.

5.3 Limitations of the current study and recommendations for further work

The following suggestions have been made to strengthen the findings of this preliminary study and increase their applicability to drinking water treatment plants.

- The results obtained in this study suggested that 'residual turbidity' will depend on ashfall grain size distribution and surface chemistry, ashfall thickness and surface water chemistry. Further work is required to better understand these relationships and improve predictive capacity for the impacts of future eruptions.

- Further work is required on optimising the dosages of chemical coagulants, particularly with respect to investigating lower dosages of alum, higher ratios of lime and a wider range of ash concentrations to better simulate different ashfall scenarios.

- To improve the applicability of this work to water treatment plants, there needs to be more integration between results obtained in this study and existing operational approaches to turbidity management utilised by water treatment plants.

6.0 ACKNOWLEDGEMENTS

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APPENDIX 1   COMPOSITION OF RUAPEHU CRATER LAKE WATER

Table A1   Composition of Ruapehu Crater Lake water from April 2010 (kindly supplied by GeoNet).

Ruapehu Crater Lake	Lab. Reference No. Collection Date Sample ID Field ID	1001714 10/04/2010 RU1000 NORTH VENT	1001715 10/04/2010 RU1000 CENTRAL VENT	1001716 9/04/2010 RU1000 OUTLET
Collection Temperature	°C	21.4	21.3	20.0
Analysis temperature	°C	19	19	19
pH		1.13	1.13	1.15
pH/ Date Analysed		14/04/2010	14/04/2010	14/04/2010
Lithium	mg/L	0.75	0.79	0.77
Sodium	mg/L	624	631	636
Potassium	mg/L	109	107	106
Calcium	mg/L	794	836	836
Magnesium	mg/L	984	1013	1013
Chloride	mg/L	5234	5525	5434
Sulphate	mg/L	7642	7840	7492
Boron	mg/L	18.2	18.6	17.2
Silica (as SiO_2)	mg/L	312	364	512
Sulphide (total as H_2S)	mg/L	0.03	0.01	0.32
H_2S/Date Analysed		13/4/2010	13/4/2010	13/4/2010
Aluminium	mg/L	353	372	370
Arsenic	mg/L	<0.015	<0.015	<0.015
Bromide	mg/L	8.8	8.8	8.9
Fluoride	mg/L	118	119	128
Iron	mg/L	353	359	357
Ammonia (total as NH_3)	mg/L	13.6	14	14.2
Oxygen 18	‰	0.32	0.3	0.35
Deuterium	‰	-31.5	-29.6	-30.7
Ionbalance		3.5	2.7	3.2

APPENDIX 2   SYNTHETIC ASH METHOD

Quantitative volcanic ash vulnerability analysis should use pristine volcanic ash, ideally so that acidic gas condensates and soluble salts attached to recently erupted ash are still present.   However, these requirements create considerable logistical and financial challenges to collect sufficient ash for laboratory testing. The locations of active volcanoes are not always conducive to collection of a sufficient quantity of ash needed for the study, and even if the ash could be collected and transported, MAF biosecurity regulations also make importing erupted ash for the study from overseas impractical. A further issue is that fresh ash surface coatings are thought to be unstable (Jones and Gislason, 2008) decaying in situ even if kept unhydrated.

Because of these issues, the Volcanic Ash Testing Laboratory at University of Canterbury has been developing a 'synthetic ash' which replicates the physical and chemical properties of fresh volcanic ash rather than relying on newly erupted material. This is based on materials that can be obtained readily in New Zealand and 'dosed' in a chemical laboratory to simulate the chemistry of fresh volcanic ash (e.g. Ruapehu) which usually contains a wide range of water-soluble elements.

The relatively simple method involves crushing and milling large quantities of Stoddard basalt from Banks Peninsula and then characterized (grain size, grain shape, density and morphology).   Broom (2010) found the 'pseudo ash' to have essentially the same geotechnical characteristics as a wide range of ashes from the Taupo Volcanic Zone.

Crater Lake water from Ruapehu was obtained and mixed with the raw synthetic ash to simulate the chemical properties of freshly erupted ash (for composition see Appendix 1). This was then left to evaporate off in an oven at ~90°C for 72 hours. Leachate from the 'doped' ash was analysed by ICP-MS and compared to those obtained from 'doped' rhyolitic ash from Tarawera, ash derived from the 2007 Ruapehu break-out lahar (Broom, 2010) and fresh ashes from overseas to ensure the synthetic ash was similar to freshly erupted volcanic ash before it is used for corrosion testing. Results indicated the synthetic ash and fresh ashes were very similar (Broom, 2010). Full details of the preparation and doping techniques are given in Broom (2010).