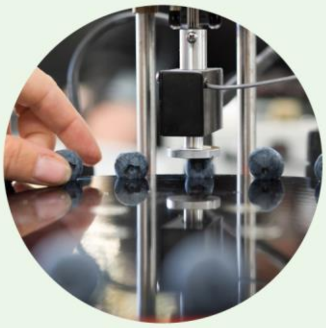







PFR SPTS No. 21829

Effects of emissions-to-air from the Ravensdown Napier Fertiliser Works on vegetation

Trolove S: Reviewed by Searle B, Clothier B, Doley D

November 2021

Confidential report for:

Ravensdown Limited

PUBLICATION DATA

Trolove S: Reviewed by Searle B, Clothier B, Doley D. November 2021. Effects of emissions-to-air from the Ravensdown Napier Fertiliser Works on vegetation. A Plant & Food Research report prepared for: Ravensdown Limited. Milestone No. 86147. Contract No. 38177. Job code: P/441018/01. PFR SPTS No. 21829.

Report prepared by:

Stephen Trolove
Scientist, Cropping Systems & Environment
November 2021

Report approved by:

Paul Johnstone
Science Group Leader, Cropping Systems & Environment
November 2021

Document control

Title: Effects of emissions-to-air from the Ravensdown Napier Fertiliser Works on vegetation				
Date	Version	Prepared by:	Reviewed by:	Approved by:
December 2020	1	S Trolove	Searle B, Clothier B, Doley D	P Johnstone
November 2021	2	S Trolove	Searle B, Clothier B, Doley D	P Johnstone

Contents

Executive summary

Effects of emissions-to-air from the Ravensdown Napier Fertiliser Works on vegetation

Trolove S
Plant & Food Research Hawke's Bay

Reviewed by Searle B[1], Clothier B[2], Doley D[3]
Plant & Food Research: [1]Hawke's Bay, [2]Palmerston North; [3]Indooroopilly, Queensland, Australia

November 2021

This report was written at the request of Ravensdown Limited (hereafter referred to as Ravensdown) as a supporting document to be submitted to the Hawke's Bay Regional Council as part of the application to renew their resource consent to discharge contaminants into air (AUTH-115256-04/DP050561Ab) from their fertiliser factory at Awatoto, Napier (hereafter referred to as the Napier Works).

The main contaminants discharged to air from the Napier Works that have the potential to harm plants are fluoride (F), sulphur dioxide (SO_2), acidic aerosols and dust. The potential effects of these at high concentrations are:

- Fluoride: leaf deformities, yellow or dead patches on leaves, reduced fruitset and reduced plant growth.
- Sulphur dioxide: leaf damage.
- Acidic aerosols: leaf deformities, burn-like symptoms and impaired stomatal behaviour.
- Dust: reduced photosynthesis, blocked stomata, increased leaf temperature and water loss.

The assessments undertaken to investigate the risk of harm included:

- Investigating any complaints made to Ravensdown over the current resource consent period (2007–2021).
- Conducting field walks of the Waitangi Regional Park, and leaf testing to investigate the cause of possible damage from emissions.
- Examining the leaf F monitoring data collected by The New Zealand Institute for Plant and Food Research Limited (Plant & Food Research) from 2007 to 2021.
- Comparing modelled F and SO_2 concentrations with guideline concentrations for vegetation published by the Ministry for the Environment (MfE).

- Reviewing the scientific literature for recommended concentrations in the case of acidic aerosols, where MfE guidelines did not exist.

The results of these assessments were:

- No cases of damage to vegetation during the current resource consent period that could be attributed to the Napier Works.
- Dust was considered to have negligible effect on vegetation outside of the Napier Works' boundary.
- There were no high leaf F concentrations that may indicate loss of marketable yield (i.e. loss of yield or quality that may affect grower returns).
- Modelled concentrations of F and SO_2 were below concentrations likely to cause economic damage to crops in the Awatoto–Meeanee area, given the current distribution of crop species.
- The F emissions may be a cause for concern if F-sensitive species are planted closer than 1.0 km to the Napier Works Manufacturing Stack, and Ravensdown emit F at the maximum rate of 1.0 kg/h for approximately 12 h or more.
- The literature review indicated that a pH of >2.7 for Manufacturing Stack emissions should be generally appropriate to avoid damage to vegetation and fruit from acidic aerosols. However, there might be a very low risk of some damage arising from regular, intermittent exposure to acidic emissions of pH ≤4.0 (depending on the crop species and growth stage) under misty or highly humid conditions without significant rainfall (≤0.2 mm), where the wind is fluctuating back and forth across orchards for several hours. This risk may be greater during flowering in spring. There have been no reports of damage under such conditions during the current resource consent period.

Suggested approaches to mitigate risks:

The low risk of potential damage if a F-sensitive crop was planted closer than 1.0 km to the Manufacturing Stack would be mitigated by:

- Management of fugitive emissions will be reduced via the proposed Source Control Plan.
- Normal factory operations release F at much lower rates (an average of 0.07 kg/h) than the 1.0 kg/h rate for 12 h used in the model.

The very low risk of damage from acidic aerosols at pH <4.0 with repeated exposure could be mitigated by:

- Adjusting the Manufacturing Stack emissions to pH >4.0 under misty or very humid conditions where the wind was blowing towards an orchard for a period greater than 30 minutes. These weather conditions are described in Condition 39 of the current consent: i.e. the pH should be adjusted to >4.0 when the wind speed is <3 m/s and the wind direction is between 030° and 155° (i.e. on-shore) and the temperature is >22°C, it is dark and the relative humidity is >70%. This condition would only hold during the growing season for pipfruit and stonefruit (late August to end of April). For the growing season outside of the flowering period (i.e. from November to April) the risk is only for multiple exposures, so emission pHs of <4.0 on up to 3 different days should not be considered a breach of resource consent.

- No other significant risks were identified.

For further information, please contact:

Stephen Trolove
Plant & Food Research Hawke's Bay
Private Bag 1401
Havelock North 4157
NEW ZEALAND

Tel: +64 6 975 8889
DDI: +64 6 975 8917
Email: Stephen.Trolove@plantandfood.co.nz

1 Introduction

This report was written at the request of Ravensdown Limited (hereafter referred to as Ravensdown) as a supporting document to be submitted to the Hawke's Bay Regional Council (HBRC) as part of the application to renew their resource consent to discharge contaminants into air (AUTH-115256-04/DP050561Ab) from their fertiliser factory at Awatoto, Napier (hereafter referred to as the Napier Works).

The purpose of the report is to determine whether the emissions from the Napier Works are currently causing damage to vegetation, and also to assess the risk of future damage. The report begins by providing essential background information – identifying the main pollutants of concern in emissions-to-air from the Napier Works that might harm vegetation and investigating whether these have caused harm during the current consenting period. To assess whether harm has been caused, this report examines the findings of the site monitoring and leaf fluoride (F) concentration sampling that has been conducted at various orchards in the Meeanee region throughout each season since the current consent was issued. Complaints of damage to vegetation that allege the Napier Works was the cause are also examined, from the date that the current resource consent was issued on 22 March 2007 until the present. Detailed investigations of the only two complaints alleging damage from airborne emissions from the Napier Works made since the pH of the Manufacturing Stack emissions was adjusted to ≥2.7 in 2008, are provided in Appendix 1. Appendix 2 describes site visits to the Waitangi Regional Park in July 2020 and September 2021 to investigate whether there were any visible signs of emissions damage. An inventory of the main commercially cultivated plant species in the area surrounding the Napier Works is provided, whether these species are sensitive to F, where these are grown, and any significant changes in crop species and distribution are noted since the current resource consent was issued.

Against this background information, the atmospheric F and sulphur dioxide (SO_2) concentrations modelled by Tonkin & Taylor (Chilton 2021) are compared against the guidelines established by the Ministry for the Environment (MfE) for their effects on vegetation, and conclusions are drawn concerning the potential risk of current emissions.

2 Airborne pollutants emitted from the Napier Works

There are three potential sources of emissions-to-air that may harm vegetation: (i) the Manufacturing Plant, which makes superphosphate fertiliser from phosphate rock; (ii) the Acid Plant, which produces concentrated sulphuric acid; and (iii) the Bradley mills and rock and superphosphate storage sites, which produce dust. Further details of these sources and the pollutants discharged can be found in Chilton (2021).

2.1 Pollutants from the manufacturing plant

The stacks of the Manufacturing Plantemit several substances into the atmosphere that may affect plant growth. These are mainly acidic vapours and aerosols, and various fluoride (F) species, with low concentrations of SO_2 (Kingett Mitchell Limited 2005). The F species emitted by the Napier Works are listed as gaseous silicon tetrafluoride (SiF_4), hydrogen fluoride (HF) and fluorosilicic acid (H_2SiF_6). According to Trail & Murray (2005), the main acid species emitted from the Manufacturing Plant is hydrofluorosilicic acid (H_2SiF_6), closely followed by SiF_4 gas, which readily hydrolyses to form more H_2SiF_6. Also present is hydrogen fluoride (HF), either dissolved in water as hydrofluoric acid, or as a gas, which readily hydrolyses in water to form more hydrofluoric acid. Small quantities of sulphuric acid and phosphoric acid are also likely to be found. Hence almost all the acids emitted from the Manufacturing Stack are fluoride-containing acids.

2.2 Pollutants from the acid plant

The main pollutant emitted from the Acid Plant is SO_2 gas, with much smaller amounts of sulphur trioxide (SO_3) and sulphuric acid aerosols (Chilton 2021). The Napier Works releases SO_2 at approximately 1.7 kg SO_2/t H_2SO_4, which is below the International Finance Corporation - World bank guideline of 2 kg SO_2/t H_2SO_4 (Chemetics® 2021). The SO_2 emissions are not believed to be a source of acidity that would have harmful effects on vegetation in the Awatoto area, since the conversion of SO_2 to acid is a reaction that will only take place in the upper atmosphere (Trail & Murray 2005). This would result in minimal deposition immediately around the Napier Works. Acidic emissions from the Acid Plant would come primarily from the release of gaseous SO_3 that is not recovered from the final absorption tower (Kingett Mitchell Limited 2005) and sulphuric acid aerosols. This SO_3 rapidly dissolves in water, which is emitted at the same time, to form more sulphuric acid aerosols. The Napier Works currently emits approximately 0.007 kg SO_3/t H_2SO_4, which is one-tenth of the IFC/World Bank Group guideline value of 0.075 kg SO_3/t H_2SO_4 (Chemetics 2021).

During cold start-ups the emission rates of SO_2 had historically been considerably greater than normal discharge rates. However, implementation of best-practice changes reduced the spike in SO_2 emissions to concentrations no greater than those of normal operating conditions (Chemetics 2021). The amount of acid emitted from the Acid Plant is low compared with that emitted from the superphosphate Manufacturing Plant (Den scrubber stacks), with acid emissions from the Acid Plant being only 1% of those from the Manufacturing Plant in a test reported by Trail & Murray (2005). This suggests that the risk of damage to vegetation from Acid Plant emissions is much lower than from the Manufacturing Plant.

2.3 Pollutants from storage sites and Bradley mills

Dust also arises from the Napier Works (Chilton 2021). This arises from the Bradley mills, which grind the phosphate rock, and from wind erosion of the storage piles of phosphate rock and superphosphate. Other sources include vehicle movements and the loading and unloading of materials.

3 Pollutants: their effects, and are they a cause for concern?

This section begins by outlining the general effects of the pollutants at high concentrations as described in the scientific literature. This is followed by a section outlining whether these pollutants are a cause for concern at the concentrations at which they are emitted from the Napier Works. Pollutants discussed are acidic aerosols, SO_2, F and dust.

3.1 Acidic aerosols

3.1.1 Effects on vegetation

A review of the scientific literature on the effects of acid in precipitation (Cape 1993) found that acidic mists or aerosols may cause acute damage to vegetation, but that acute damage should not occur from acidic rainfall because the concentration of acid was believed to be too low. Acidic mists can cause leaf deformities and burn-like symptoms on leaves where the droplets coalesce and settle (Searle et al. 2007a), as well as impairing stomatal behaviour (Cape 1993). Acidic mists also enhance the wettability of leaves in some species (Cape 1993), which may enhance the entry of acid, and other ions, into the leaves. Young leaves are more susceptible to acid damage than mature leaves (Jacobson 1991). Leaching of cations has also been observed in leaves exposed to acid mists (Cape 1993), but this effect is minor and unlikely to have any economic consequence on crop production (Doley 2006a). Plants under nutrient stress may be more affected by acidic mists than plants with adequate nutrition (Cape 1993), and plants exposed to acidic mists may be more susceptible to frost damage (Fowler et al. 1989).

Symptoms of acidic aerosol deposition may include discrete necrotic spots 2–3 mm in diameter (Doley 2006b). Where these droplets coalesce, the necrosis may be evident at the drip points or lowest points on the leaves (Figure 1) or fruit (Figure 2). Within a canopy, the uppermost leaves, or leaves on the windward side may be expected to show more damage than leaves lower in the canopy, or those on the leeward side. Similarly, within an orchard or field, plants nearest the source of acidity, or in exposed locations, such as gaps in shelterbelts, may be expected to show more symptoms than plants in a more sheltered location.

Figure 1. Leaves on a kiwifruit vine from Dewar's orchard. The upper leaf shows spot necrosis, and there are two necrotic spots on the lower leaf that may have been caused by drainage of liquid from the upper leaf. The damage was attributed to wet acidic deposition (Doley 2005). Photo taken by Ravensdown staff on 6 January 2005. Source: Doley (2006b).

Figure 2. 'Pacific Beauty' apples from Plumpton Park Estate, early 2004. Fruits 1, 2 and 5 show evidence of drip point injury. Fruit 3 shows injury associated with contact with a branch, and fruits 4 and 6 show evidence of contact between adjacent fruits. Acidic emissions from the Napier Works might have contributed towards the observed drip point injury (Doley 2005, 2006a).

3.1.2 Are acidic emissions from the Napier Works a cause for concern?

Acidic emissions come mainly from the Manufacturing Plant, as predominantly F-acid species, but also from the Acid Plant via SO_3 emissions. Kingett Mitchell Limited (2005) reported that SO_3 was emitted from the Acid Plant at the rate of approximately 1 kg/h, which they described as “low” and is expected to have a “minor potential for any adverse effects”. The recent long-term average emission rate of SO_3 and H_2SO_4 combined, from 1 January 2015 to August 2021, was 0.8 kg/h (Chilton 2021), which would make the risk of adverse effects of acidity from the Acid Plant very low. The majority of the acidity emitted by the Napier Works comes from the Manufacturing Plant (Section 2.2). In the previous resource consent period (prior to 2007), emissions from the Manufacturing Stack were as low as pH 2.0 and there were reports of damage to vegetation that were likely to have come from the Ravensdown plant (e.g. Doley 2005; Figure 1). Since 2008, the pH of emissions from the Manufacturing Stack has been adjusted to ≥2.7 and there have been no reports of damage attributable to the Napier Works (Section 4).

There is no guideline from the MfE for the pH of acidic emissions to air, against which to compare emissions from the Napier Works. There has been considerable research done in Europe and North America to develop environmental limits for acidic emissions. This was to protect plants from damage, based on the risk of soil acidification. The risk of damage resulting from soil acidification was deemed to be low in New Zealand (Stevenson et al. 2000), and therefore MfE (2002) decided not to set a guideline for acid emissions. Since no limit has been set for New Zealand, a review of the scientific literature was undertaken to establish what concentration of acidity may be a cause for concern; the main findings are presented below.

Jacobson (1991) reviewed the effects of acidic mists on crop plants and concluded that the threshold pH for foliar injury was generally below 3, but that under some conditions injury could occur above 3. Different plant species show different tolerance to acidic mists. For example, watermelons were unaffected by simulated acid rain at pH as low as 2.5; whereas in the same experiment, capsicums showed a yield reduction in fruit fresh weight and fruit number of approximately 20% at pH 3.5 (Choi et al. 2010). Grasses are relatively tolerant of exposure to acidic mists, with no observed injury in upland grasses after exposure to mist with a pH of 2.5 (Ashenden & Bell 1987, Ashenden et al. 1991). Grasses generally receive lower doses of acidity than trees, since trees have a large aerodynamic roughness and may capture up to four times more droplets from acidic mists than grass (Fowler et al. 1990). For forest trees, the order of sensitivity to damage by acidic mists is generally: herbaceous dicots > woody dicots > monocots > conifers (Percy 1991). Jacobson (1991) reviewed the effects of simulated acid rain (ranging in pH of generally <3 to ~5) on crops and found no effect on the growth or yield of oats, potato and maize. Effects on soya beans were variable, with some studies finding no effect, and others showing a reduction in yield. Regardless of the effect, soya beans are not grown in the Awatoto–Meeanee area.

Experiments by Searle et al. (2007a) on apple trees on the Heretaunga Plains found no signs of visible injury on leaves receiving a single spray of sulphuric acid at pH 2.7, but did observe injury symptoms at pH 1.4. Spraying sulphuric acid of pH 2.7 had no effect on apple fruit, but fruit burning was evident at pH 1.4 (Searle et al. 2008). The acidic spray or F had no effect on fruit russeting (Searle et al. 2008). Geelen (2006a) sprayed mature *Malus domestica* ‘Braeburn’ trees bearing foliage and fruit with undiluted condensate (pH 2.7, 34 mg F/L) from the Ravensdown stack at 1500 L/ha. Two applications were made, the first early in the morning, and the second in the evening 1 week later. The trial had three replicates (one tree per replicate) and a water-only treatment was included as a control. There was no evidence of damage to fruit or foliage. Fruit from this spray trial was stored for 4 months at 0.5°C, and there was no difference between fruit sprayed with condensate and water in their rate of weight loss.

Flowers, of most plant species, are not waxy like leaves or apple fruit, and have less acid buffering capacity (McCool et al. 1990), so may be more susceptible to damage from pollutants in solution such as acidity and F. There is some evidence (p<0.07) that either acidity (sulphuric acid at pH ≤2.7) or F (34 mg/L) sprayed on apple trees during flowering reduces fruit set (Searle et al. 2008). McCool et al. (1990) found that a low percentage (<3%) of ornamental flowers (carnation, chrysanthemum and zinnia) showed signs of damage from exposure to simulated acidic fog comprised of nitric and sulphuric acid at pH of ≤3.4–4.0, and Azalea flowers at pH ≤3.6 (Musselman & McCool 1994). This was cosmetic damage, and does not give any indication of effects on yield. Van Ryn et al. (1988) examined the effects of acidic mist on the germination of red maple pollen grains on stigmas that had previously been exposed to acidic mist. They found a reduction in the percentage of pollen grains that germinated as the pH dropped from 4.6 to 3.6. The number of pollen tubes that reached the base of the style also consistently decreased with each drop of 1 pH unit below 5.6. The downward trend in pollen germination and tube growth was significant as pH decreased. This agrees with earlier work by Cox (1984) on northern evening primrose, where the LD_{50}[1] for pollen germination was pH 3.6, and for pollen tube growth was pH 4.7. The effects of acidity on pollen differ with plant species and nitric acid has been shown to have a less harmful effect than sulphuric acid (Paoletti & Bellani 1990). Munzuroglu et al. (2003) treated apple flowers with solutions of differing pH ranging from 2.9 to 6.5, and found that the germination of apple pollen decreased by 42% at pH 3.3, compared with the control at pH 6.5. In addition, pollen tube elongation reduced by 24% at pH 3.4. With pH values below 3.1 there was complete destruction of the pollen tubes. Effects of acidic precipitation at flowering on apples vary with variety. Forsline et al. (1983b) found no effects of simulated acid rain on fruitset of ‘Empire’ and ‘Golden Delicious’ apples when sprayed at flowering with solutions ranging from pH 2.5 to 5.5; however, fruitset and pollen germination was reduced in the variety ‘McIntosh’ at pH 2.5, but not at pH 3.5. Out of three grape varieties sprayed with simulated acid rain, only one showed a significant decrease in pollen viability when sprayed with a pH 2.75 solution at flowering, and none at pH 3.25, when compared with vines receiving ambient rainfall (Forsline et al. 1983a).

Despite the reports above of damage during flowering and fruitset, a review of the effects of acidic precipitation of crops concludes that “the majority of studies indicate that reproductive tissues display no special susceptibility to acidic precipitation” (Jacobsen 1991), and even if damage to flowers or reduced fruitset occurs, this does not necessarily translate into a decrease in yield. One reason for this is that many fruit-crops require thinning of flowers and/or immature fruit. Another reason is that fruit size increases as number of fruit decreases. Forsline et al. (1983a) sprayed five grape varieties with simulated acid rain (pH 2.75) at flowering, which reduced pollen germination in three cultivars. However, fruitset was reduced in only one of these varieties, which was said to have no effect on economic yield, since this variety required thinning. Two peach varieties were sprayed with sulphuric acid with pH values of 2, 3, 4, 5, with a control receiving ambient rainfall at pH 6 (Klymenko & Klymenko 2003). Trees were sprayed monthly from full flowering until leaf-fall. There was no damage observed after the first spray. Damage was observed after the second spray and fruit yield was reduced by 27% in one variety at pH 2, and by 59–51% in the more sensitive variety at pH 2 and 3, with no effect at higher pH. The lower yields were the result of both smaller fruit and, to a greater extent, a reduction in number of fruit per tree.

[1] LD_{50}: the lethal dose at which 50% of the organisms die in response to a chemical treatment, so in this case, the dose of acidity at which half of the pollen fails to germinate.

Repeated intermittent exposure to acidic mists may be more harmful than continuous exposure. Experiments that involve repeated intermittent exposure to acidic mists have recorded plant damage with solutions of higher pH (less acidic) than other experiments where the same plant species was continuously exposed to the same acid. For example, Jacobson et al. (1990), documented mild visual injury symptoms in red spruce after 59 exposures to sulphuric acid at pH 3.5, whereas Taylor et al. (1986) and Laurence et al. (1989) found no evidence of damage to red spruce with shorter duration exposures to sulphuric acid of pH 3.5 without repeated wet-dry cycles or fluctuating acidity. Repeated exposure may have resulted in an increase in the concentration of acid on the leaf surface. Exposure to sulphuric acid mist also causes extensive 'erosion' of surface waxes in some species (Rinallo et al. 1986), so perhaps repetitive exposure could have a greater effect once the cuticular wax has been 'eroded' away. However, Horntvedt (1988) studied the same species and found no change in cuticular wax, and other species even showed an increase in cuticular wax upon exposure to sulphuric acid rain. In his review of evidence, Doley (2006b) stated that sulphuric acid injures plants directly if the pH is below about 2.0 for one to four exposures, whilst 16 or more regular exposures over a growing season may result in injury at pH 3.5 or 4.0. We were not able to find a study that compared the effects of intermittent exposure versus continuous exposure to the same concentration of acid under the same conditions.

Repeated exposure to acidity may also affect crop yield and quality. Weekly sprays of acid rain at pH 3.0 during fruit development was found to delay ripening in 'Golden Delicious' apples, compared with sprays at pH 3.5 (Forsline et al. 1983b). Eighteen sprays at pH 3.0 and at pH 4.0, applied weekly to developing apple fruit, decreased fruit set, increased fruit drop, decreased fruit weight and yield, and increased russeting compared with treatments receiving deionised water or ambient rainfall (Rinallo 1992). Fruit exposed to repetitive sprays of pH 3.0 (and to a lesser extent, those exposed to pH 4.0) also showed a decline in fruit quality, including lower dry matter, calcium, sugars and ascorbic acid (Rinallo et al. 1993). Repeated exposure to simulated acid rain (pH 2.75) has also been shown to reduce berry quality in grapes (Forsline et al. 1983a). Two varieties out of nine that were sprayed weekly (from the week before flowering) showed a significant decrease in soluble solids compared with vines receiving ambient rainfall (pH 3.3–7.0).

According to Doley (2006b), the weather conditions that gave rise to the greatest risk of damage from the Napier Works' stack emissions were misty or high humidity without significant rainfall (≤0.2 mm), because >0.2 mm will cause runoff and wash the acidity from the leaf surface. Under these conditions, evaporation of stack emissions would occur slowly, and if the wind direction was fluctuating back and forth across orchards for several hours, it would give rise to multiple exposures across the orchard. These conditions may cause an increase in the concentrations of F and acidity on the leaf surface, which may enter the leaf over a significant period of time and cause damage.

There is also the possibility that acidic mists, together with F, may interact with the application of other chemicals, leading to crop damage. This may have been the case with an application of Hi-Cane® and mineral oil preceding the arrival of an acidic mist from the Ravensdown site in September 2005, as suggested as a possibility by Doley (2005) and AgFirst Consultants (2005).

Kingett Mitchell Limited (2005) concluded that, since there was a significant reduction in F emissions from the Napier Works after April 2004, wet acidic deposition was the most likely mechanism for causing injury to crops from discharges from the Napier Works. In response to this possibility, the operating procedures at the Napier Works were modified in February 2006 to cease the manufacture of fertiliser under specified meteorological conditions that might lead to the wet deposition of acid. Doley (2006b) stated that since those conditions were implemented, there have been no instances of injury attributable to the Napier Works. In addition, the most likely source of acidic emissions were the

Den stacks, so it was therefore proposed that the pH of the emissions from these stacks be raised to >2.7. This work was completed in 2008, and Ravensdown report that the average pH of emissions from the three Manufacturing Stacks for the period 2 October 2020 to 10 October 2021 was 3.7 (Reuben Manson, Ravensdown, pers. comm., October 2021). Since the adjustment of the pH of the Manufacturing Stack emissions, there has been only two complaints, that Ravensdown is aware of, alleging acid burn. This is addressed in Appendix 1, and it was concluded that the observed symptoms were not the result of acid burn.

This review of the scientific literature has identified a theoretical risk of acidic emissions at pH <4.0 during flowering and under conditions of a large number of repetitive exposures. However, the crucial information missing from many of these studies, so that any effects can be modelled and the risk assessed, is the amount of acidic water per unit area. This omission from studies was identified back as far as 1989 (Klemm 1989), but it appears that this request has been largely ignored by the scientific literature. Most studies are likely to have applied liquid until close to run-off, which is likely to be far more liquid than what trees located >1.5 km from the Napier Works might receive. The effects of acidic mists on vegetation at reduced water rates do not appear to have been studied. In the absence of water-rate information, recommendations have been made on the basis of pH alone, which are likely to overestimate the amount of acid received by vegetation around the Napier Works, and therefore be overly conservative.

In conclusion, it appears that a pH of >2.7 for stack emissions should be generally appropriate to avoid damage to vegetation and fruit by acidic aerosols, as is required by the current resource consent conditions (AUTH-115256-04 / DP050561Ab). There are two situations where there is a small risk of damage occurring at a pH of 2.7: one is when wind is blowing over the orchards during flowering, and the second is under misty or highly humid conditions without significant rainfall (≤0.2 mm) with regular, intermittent exposure. During flowering there may be some reduction in pollination or fruitset for some varieties, but this is not likely to result in a decrease in yield since most fruit crops require thinning. To mitigate this small possible risk of damage from acidity, the pH should be maintained above 4.0.

The fact that injury from stack emissions has not been documented since the pH of the Den scrubbers was increased, suggests that either these meteorological conditions are extremely rare, or that the pH of ≥2.7 is sufficient to avoid damage in the crop varieties planted in the Awatoto–Meeanee area. Alternatively, now that Ravensdown is adjusting the stack emissions to approximately 3.7 (rather than 2.7), and now that it has average F emissions of 0.07 kg/h (Section 3.3.8), these practices have mitigated any risk of damage. The construction of the proposed 50 m Manufacturing Stacks should further mitigate any risk of acid damage, since atmospheric modelling by Chilton (2021) shows that these changes will reduce atmospheric F concentrations, which also means a reduction in acidity, since the F compounds emitted are acid-forming species (see Section 2.1).

3.2 Sulphur dioxide

3.2.1 Effects on vegetation

Sulphur dioxide (SO_2) entering the leaf is oxidised in the chloroplast in the presence of light, producing oxyradicals, which can damage the leaf (Okopudu et al. 1996). At lower concentrations of SO_2, these oxyradicals are detoxified by the action of antioxidant enzymes and damage is avoided, but at high concentrations (>1400 µg/m^3 over 24 h) the capacity of the plant's antioxidant system is exceeded, and damage occurs (Bressan et al. 1979). In addition, under certain conditions, SO_2 may dissolve in water, either in the atmosphere or on moist surfaces inside the plant (Doley 2006a), and oxidise slowly to sulphur trioxide (SO_3), which will rapidly react with water to form sulphuric acid.

3.2.2 Are sulphur dioxide emissions from the Napier Works a cause for concern?

Guidelines for maximum allowable atmospheric concentrations of SO_2 were published by the MfE (2002), and these are shown in Table 1. These concentrations are 30 µg/m^3 for agricultural crops and 20 µg/m^3 for forests and native vegetation, averaged over 1 year. Conservative modelling was conducted by Chilton (2021), based on annual average results derived from the 75th percentile of measured in-stack concentrations (i.e. above average concentrations). This modelling indicated that the highest SO_2 concentrations would be less than one-tenth of the 30 µg/m^3 annual guideline for agricultural crops, and less than one-quarter of the annual guideline for the most sensitive vegetation – lichens (Figure 3). Short-term modelling was also carried out by Chilton (2021), assuming that the Napier Works was producing SO_2 at the maximum rate permitted by the current resource consent (60 kg SO_2/h for 1 or 24 h). This modelling (Figure 4 and Figure 5) also showed that the highest atmospheric SO_2 concentrations emitted were less than the critical concentrations for 1 and 24 h given in the MfE guidelines (Table 1). Chilton (2021) also made it clear that the modelled numbers in Figure 4 and Figure 5 assume that the Napier Works was operating at peak production rates (at the 99.9th percentile), whereas almost all of the time the concentrations will be lower than this. Furthermore, planned upgrades of the Acid Plant converter will lower SO_2 emissions even further and a limit of 40 kg SO_2/h for 1 h average has been proposed in the Ravensdown Air Discharge Strategy, as indicated by the modelling of Chilton (2021). The modelling therefore indicates that SO_2 emissions from the Napier Works are not a cause for concern, which agrees with the conclusion of Doley (2005, 2006a).

Table 1. New Zealand ambient air quality guidelines for plants showing the maximum allowable concentration (critical level) of sulphur dioxide for selected averaging times (MfE 2002).

Maximum allowable concentration (µg/m^3)	Averaging time	Applicability
350	1-hour	Human health and ecosystems
120	24-hour	Human health and ecosystems
30	Annual and winter average	Agricultural crops
20	Annual and winter average	Forests and natural vegetation
10	Annual	Lichens

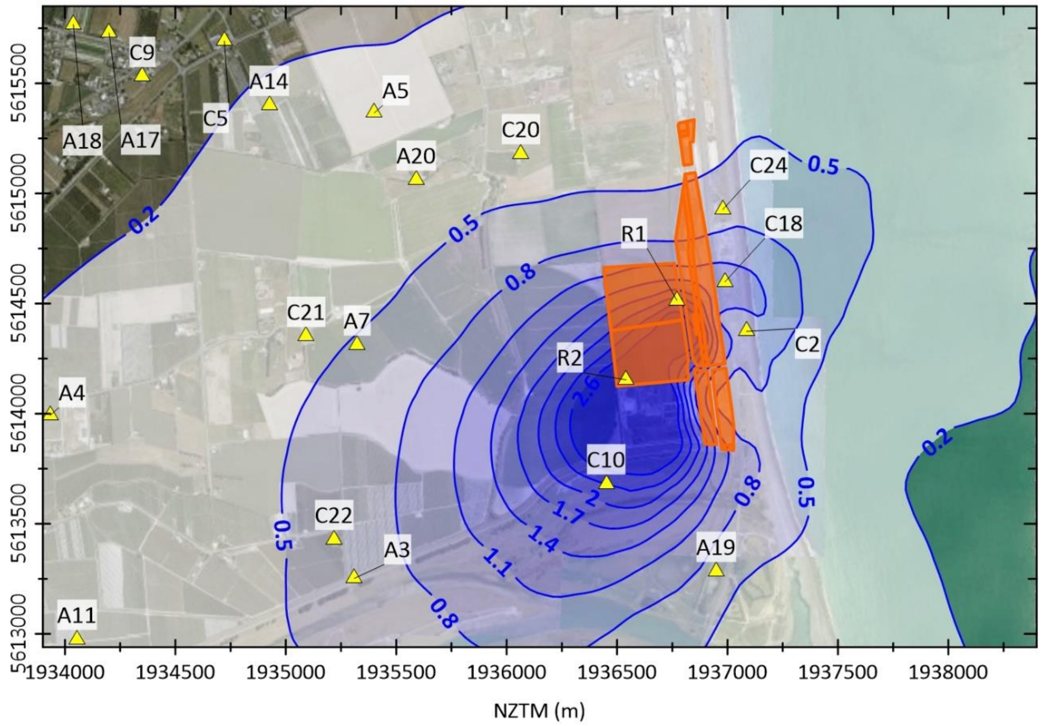

Figure 3. Predicted annual sulphur dioxide atmospheric concentrations (µg/m^3) at ground level in the area surrounding the Napier Works – based on the 75th percentile of stack data testing. Figures include site emissions only. Ravensdown-owned land is shaded orange. Source: Chilton (2021). The yellow triangles are locations of special interest for the Chilton report.

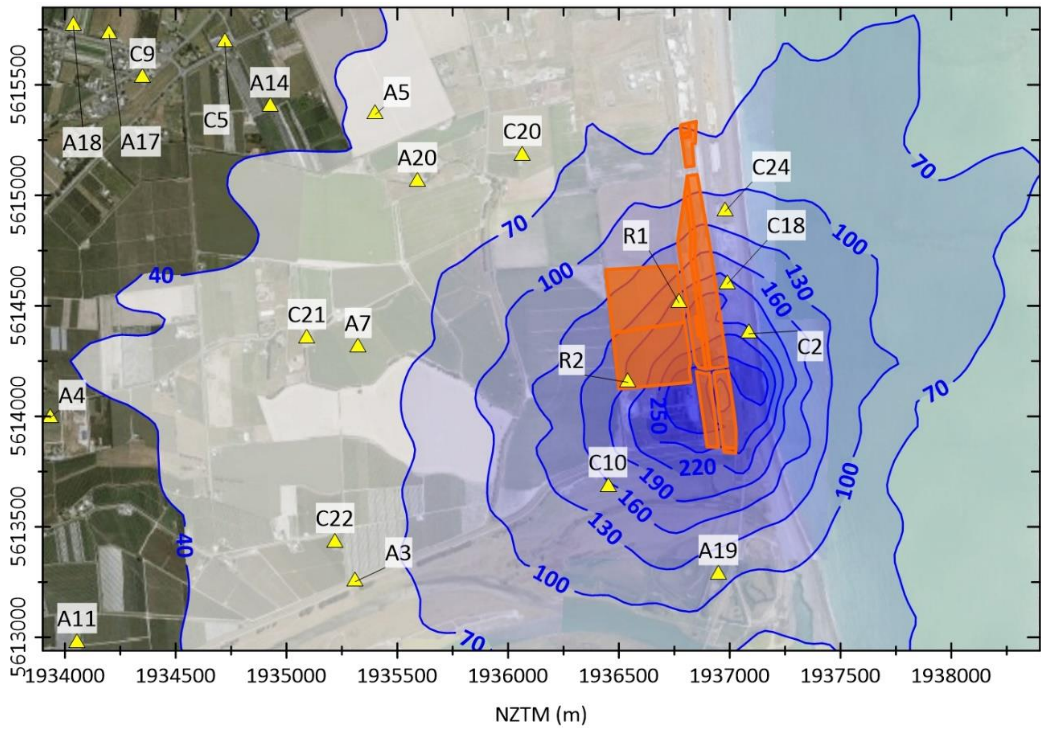

Figure 4. Predicted maximum (modelled 99.9th percentile) 1-h average atmospheric sulphur dioxide concentrations (µg/m^3) at ground level around the Napier Works – based on the peak emission rate allowed by the current consent of 60 kg/h. Only emissions from the Napier Works are accounted for. Ravensdown-owned land is shaded orange. Source: Chilton (2021). The yellow triangles are locations of special interest for the Chilton report.

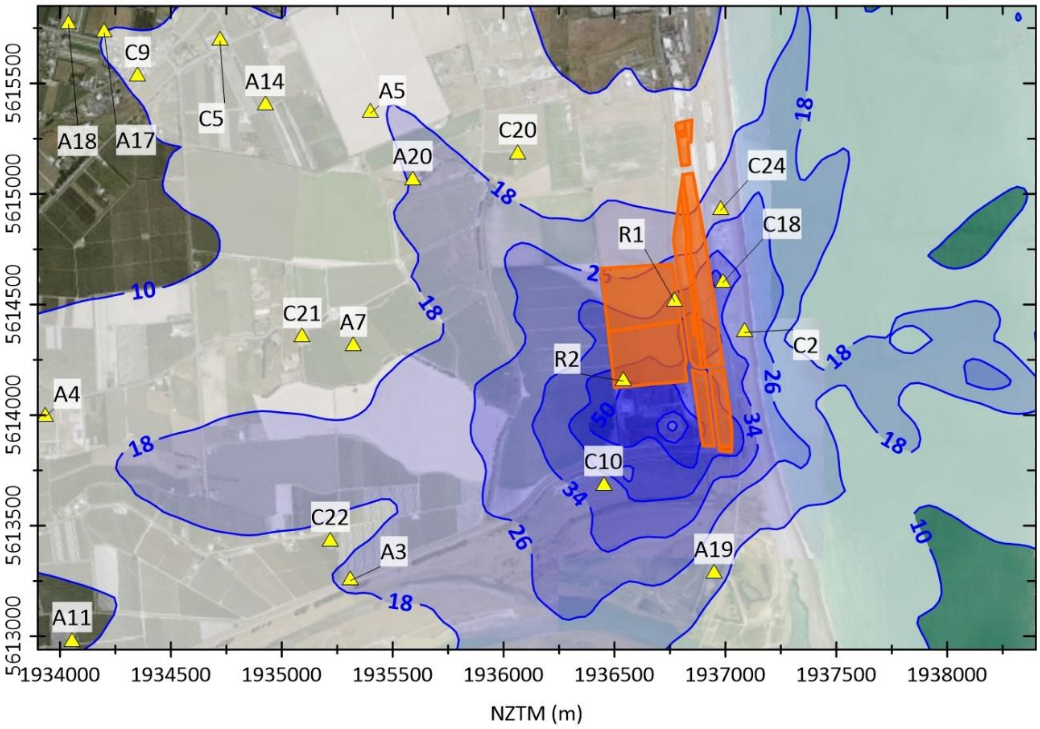

Figure 5. Predicted maximum 24-h average atmospheric sulphur dioxide concentrations (µg/m^3) at ground level around the Napier Works – based on the peak emission rate allowed by the current consent of 60 kg/h. Site emissions are accounted for only. Ravensdown-owned land is shaded orange. Source: Chilton (2021). The yellow triangles are locations of special interest for the Chilton report.

3.3 Fluoride

3.3.1 Effects on vegetation

The effects of atmospheric F on plants have been described in detail by Doley (1986) and Weinstein & Davison (2004), and in the reports and evidence supporting the Ravensdown 2005 resource consent application on the effects of atmospheric F on horticultural crops (Doley 2005, 2006a). These documents explain that F is highly toxic to plants and may have acute or chronic (longer term exposure) effects. Symptoms that may arise from F toxicity are outlined in Table 2. In addition to direct damage to plants, exposure to F may also increase the susceptibility of plants to other stresses such as insect damage (Edmunds 1983) or increased disease (Laurance 1983). These symptoms are only mentioned briefly here, since some symptoms had been observed during the previous resource consent period, but not the current one. Since 2007, no F toxicity symptoms have been observed to our knowledge, presumably because the amount of F emitted into the atmosphere is now much lower (Section 3.3.8).

Table 2. Symptoms that may arise from fluoride toxicity.

Plant part	Symptoms	Reference
Leaves	Chlorosis (yellowing)	Doley 2005
	Deformation, stunting	Doley 2005
	Necrosis (dead tissue, which resembles burn-like symptoms in the case of F toxicity)	Doley 2005
Flowers	Inhibition of pollen germination or pollen tube growth	Dinh et al. 1973
	Reduced fruitset	Searle et al. 2007b
Whole plant	Reduced growth (sometimes without other visual symptoms being evident)	Doley 2005

An additional point worth noting is that the risk of F toxicity to plants via soil uptake in the Awatoto–Meeanee region is negligible, since F in soil is largely unavailable to plants because it is very strongly bound to soil organic matter (Weinstein & Davison 2004).

3.3.2 Guidelines for atmospheric fluoride concentrations

In determining whether the F emissions are of concern, it must first be decided whether the amounts of these substances exceed critical values known to cause damage to plants. Critical concentrations for F emissions have been published by the MfE (2002), above which plant growth may be affected (Table 3). These guidelines account for the fact that plants may be damaged by lower concentrations of F if they are exposed to F for a longer time, since F is a cumulative toxin to plants (Section 2.2). Dr David Doley was involved in discussions that led to the development of these MfE limits in Table 3, and he provided an explanation for the development of these guidelines in evidence submitted to the HBRC at the previous resource consent hearing (Doley 2005). Much of that information does not need to be repeated here, suffice to say that the application of these guidelines would not mean that no F damage was observed, but rather the grower would not experience any detectable economic loss. Since economic returns depend on both yield and quality, consideration of effects on both yield and quality have been included in the development of these guidelines. Doley et al. (2003) reports that adherence to these guidelines in Australia has prevented the occurrence of detectable effects on yield and quality of grapevines. This conclusion was reinforced by a 30-year study in the Hunter Valley, Australia, that found no reports of grape vine yield loss at vineyards that met the air quality guideline of a 90-day mean ambient F concentration of 0.25 μg/m^3 or a January foliar F concentration of less than 50 mg/kg (Doley & McNaughton 2014).

Table 3. New Zealand ambient air quality guidelines for plants showing the maximum allowable concentration (critical level) of fluoride (F) for selected averaging times (MfE 2002).

Applicability	Critical F concentration (μg/m^3)	Averaging time
General Land-Use	3.7	12-hour
	2.9	24-hour
	1.7	7-day
	0.84	30-day
	0.5	90-day
Special Land-Use	1.8	12-hour
	1.5	24-hour
	0.8	7-day
	0.4	30-day
	0.25	90-day
Conservation Areas	0.1	90-day

3.3.3 Fluoride-sensitivity of different plant species

With regards to which classification is applicable to the land uses in the area surrounding the Napier Works, the General Land-Use classification (Table 3) is deemed suitable for tolerant species such as pasture and most crops (Table 4). However, for sensitive crop species such as grapes, stonefruit and *Pinus radiata*, the classification of Special Land-Use is applicable (Doley 2005). The distribution of F-sensitive crops is discussed in the following section (Section 3.3.4). The category with the lowest critical limit of 0.1 µg/m^3 is that of Conservation Area. According to Doley (2020), the low limit was established for conservation areas in order to protect species that either were extremely sensitive to F, or where F sensitivity was unknown but the species was classified as threatened and could potentially be highly sensitive to F. Coastal species are naturally exposed to quite high concentrations of F in sea spray, as shown by calculations by Doley (2008). Therefore, it is very unlikely that a coastal species would be highly sensitive to F. Doley therefore considers that the ambient F guideline for General Land-Use is appropriate for the Waitangi Regional Park, rather than the guideline for conservation areas, which is designed to protect highly sensitive plant species (Doley 2020). This issue is further discussed in Appendix 2.

Each plant species is affected differently by F, and even varieties within species have widely different tolerances to F damage. For example, the cultivar *Malus domestica* 'Golden Delicious' is known to be more susceptible to F damage than other apple cultivars (Barritt & Kammereck 1983). A list of the main crop species grown in the Awatoto–Meeanee area and their sensitivity to atmospheric F is provided in Table 4. Grapes and stonefruit are sensitive to atmospheric F (Table 4), so to protect these crops, the Special Land-Use critical concentrations for F (Table 3) are applicable to the Awatoto–Meeanee area.

Table 4. Crop species in the Awatoto–Meeanee area and their relative sensitivities to fluoride (F). Source: Modified from AgFirst Consultants (2005). No data on the sensitivity of kiwifruit to F was found in the scientific literature. Note that Davison (2005) and Doley et al. (2004) disagree over the F-sensitivity of pumpkin.

Crop	Relative sensitivity to airborne F	Reference
Apple	Intermediate	Doley et al. (2004)
Bean	Tolerant	Davison (2005)
Beetroot	Tolerant	Buse-Dragomir (2010)
Brassica vegetable	Tolerant	Davison (2005)
Grape	Sensitive	Doley et al. (2004)
Kiwifruit	Unknown	-
Leek	Sensitive	Davison (2005)
Lettuce	Tolerant	Davison (2005)
Maize/sweetcorn	Sensitive-Intermediate	Davison (2005)
Onion	Sensitive-Intermediate	Davison (2005)
Pasture	Tolerant	Doley et al. (2004)
Pea	Intermediate-Tolerant	Davison (2005)
Pear	Intermediate-Tolerant	Davison (2005)
Pinus pinea	Intermediate	Doley et al. (2004)
Pinus radiata	Sensitive	Doley et al. (2004)
Potato	Tolerant	Buse-Dragomir (2010)
Pumpkin	Sensitive	Doley et al. (2004)
Squash/pumpkin	Very tolerant	Davison (2005)
Stonefruit	Sensitive	Doley et al. (2004)
Tomato	Intermediate	Davison (2005)

3.3.4 Distribution of crop species in the Awatoto area

The concentration of F in monitored vegetation surrounding the Napier Works decreases sharply with increasing distance from the Works and approaches background concentrations at a distance of approximately 2 km from the Napier Works (Figure 9). Therefore, to be conservative, a radius of 3 km from the Napier Works was drawn and a survey of the main vegetation types within that radius was undertaken. The major land uses within that area, as indicated by the Land Cover Data Base (LCDB 2020) and modified by Google Maps, are given in Table 5. The major land uses are short-rotation cropping, grassland, and F-tolerant perennial crops. The short-rotation crops grown in the area include maize, sweetcorn, beetroot, squash, onion and tomato, and less commonly pea, bean, pumpkin, spinach and small areas of market gardening, which includes lettuce, cauliflower, leek, cabbage, broccoli and silver beet. The distribution of these various land-cover types around the Napier Works is shown in Figure 6. Most of the perennial crops are located more than 2 km from the Napier Works (Figure 6). The sensitivity of these various crops to F is given in Table 4. The F-sensitive perennial crops are located 1.9 km, or more, from the Napier Works' Manufacturing Stack (Figure 6). The types of crops and their distribution has changed little from that described by AgFirst Consultants (2005). The main difference is that 20–30 hectares of beetroot is now grown, which is tolerant to F (Table 4).

Table 5. Area (ha) of the different vegetative land-cover types in the Awatoto area. Source: Landcover database and Google Maps. Fluoride-sensitive perennial crops include grapes (1.9 ha), stonefruit (15.7 ha) and *Pinus radiata* (3.2 ha).

Grassland	F-tolerant perennial crops	F-sensitive perennial crops	Short-rotation cropland	Exotic trees	Native scrub	Herbaceous saline vegetation	Herbaceous freshwater vegetation
479.2	296.3	20.8	596.2	5.2	20.0	4.3	6.3

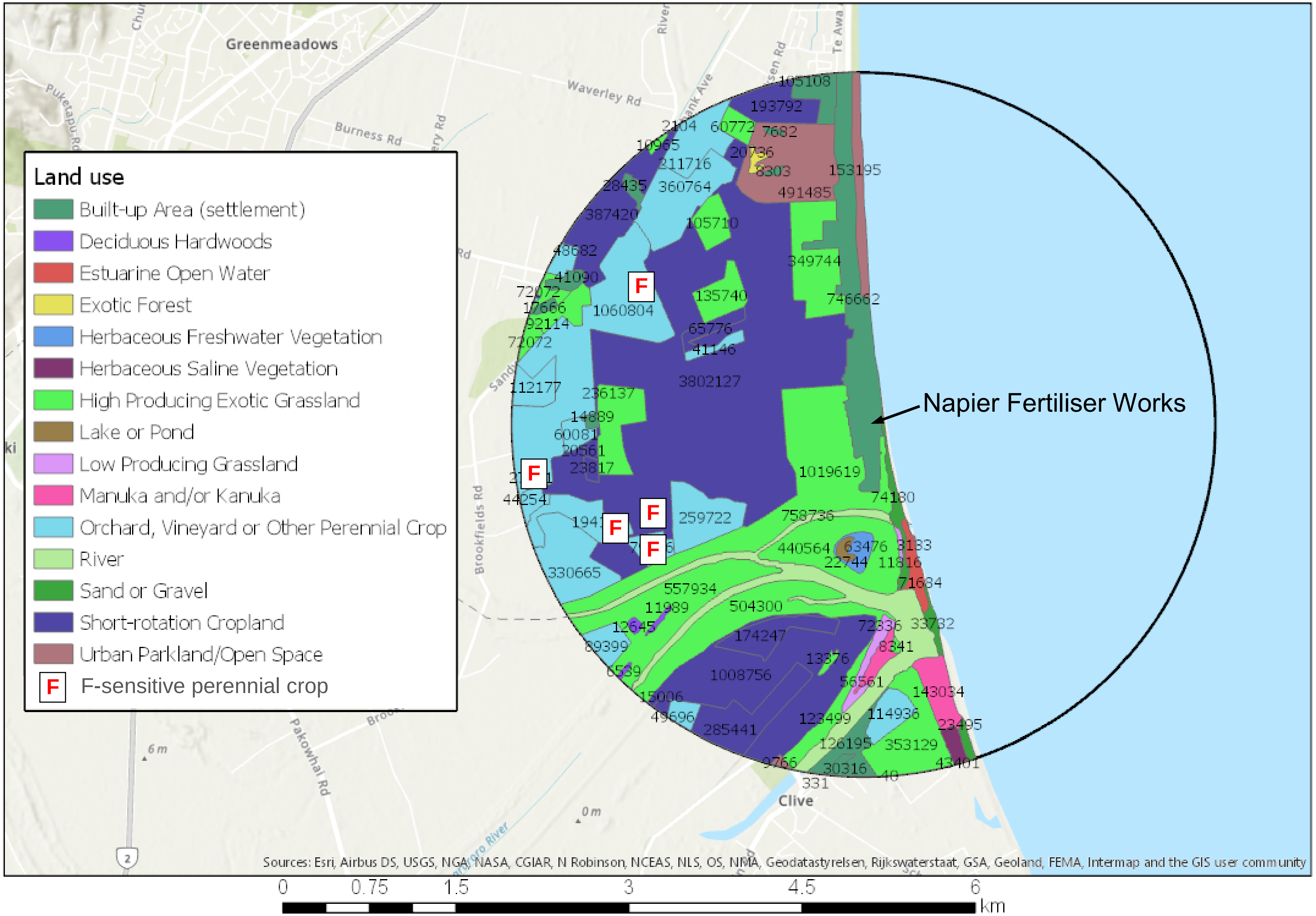

Figure 6. Land use within a 3-km radius of the Napier Works, as given by the land cover database version 5.0 (LCDB 2020). The areas of each polygon (in m^2) are given on the map.

3.3.5 Effects of fluoride on perennial crop species

Prior to the issue of the current resource consent in March 2007 there were reports of damage to perennial crops that were attributed to the Napier Works (Tate 2003, Doley 2005). Therefore, the current resource consent issued in 2007 requires regular monitoring of vegetation and foliar F concentrations from September to May at sites in the Meeanee–Awatoto area. Leaf F concentrations have been monitored in perennial crops grown in the Meeanee area by Tate (2003, 2005) and by Plant & Food Research since 2007 (Searle et al. 2009, 2011, Trolove et al. 2011, 2012, 2013, 2014, 2015, 2016, 2017, 2018, 2019, 2020). A list of the monitoring sites is provided in Table 6 and the location of these sites with respect to the Napier Works is shown in Figure 7. These sites were established in 2007, as recommended by Doley (2005), in consultation with the HBRC, and monitored by Plant & Food Research. The methodology for sampling these sites for leaf F concentrations is provided in Appendix 4. Some of these sites have been discontinued, either because the plants were pulled out, or because the concentrations measured were consistently very low, and a decision was made in consultation with HBRC and (the then) Pipfruit New Zealand to cease monitoring at these sites.

Table 6. Sites monitored by Plant & Food Research for leaf fluoride concentrations since 2007.

Site No	Site	Location	Distance from stack (km)	Plant type	Years monitored	Comment
1	Johnny Appleseed	Brookfields Rd	3.10	Apple	2007–2021	Currently monitored
2	Brookfields	Kings Road	1.53	Grape	2007–2010	Vines removed
3	Brookfields	Kings Road	1.49	Grape	2007–2011	Vines removed
4	Brookfields	Kings Road	1.49	Apple	2007–2021	Currently monitored
5	Brookfields	Kings Road	1.62	Apple	2007–2021	Currently monitored
6	Brookfields	Kings Road	1.72	Grape	2007–2012	Vines removed
7	Apollo	Tannery Road	4.72	Apple	2007–2013	Consistently low concentrations, monitoring ceased
8	Mr Apple	Meeanee Road	3.80	Apple	2007–2013	Consistently low concentrations, monitoring ceased
9	Steiner Apollo A (T&G)	Willowbank Rd	3.24	Apple	2007–2021	Currently monitored
10	Steiner Apollo B	Willowbank Rd	2.99	Apple	2007–2010	Consistently low concentrations, monitoring ceased
11	Simpkin	Awatoto Road	2.48	Apple	2007–2021	Currently monitored
12	Plumpton Park	Awatoto Road	2.21	Apple	2007–2021	Currently monitored
13	Dewar Orchard	Awatoto Road	1.97	Italian alder	2007–2021	Currently monitored
14	Dewar Orchard	Awatoto Road	1.98	Stonefruit	2009–2012	Trees removed
15	Wells Block	McLeod Road	1.60	Apple	2007–2011	Trees removed
16	Control orchard	Lawn Road	5.47	Apple	2007–2017	Trees removed
17	Maimai Creek	Brookfields Rd	2.45	Grape	2013–2016	Vines removed
18	Johnny Appleseed	King Road	2.00	Stonefruit	2013–2021	Currently monitored
19	Brookfields Winery	Brookfields Rd	3.01	Grape	2017–2021	Currently monitored
20	Control orchard	Lawn Road	6.47	Apple	2018–2021	Currently monitored

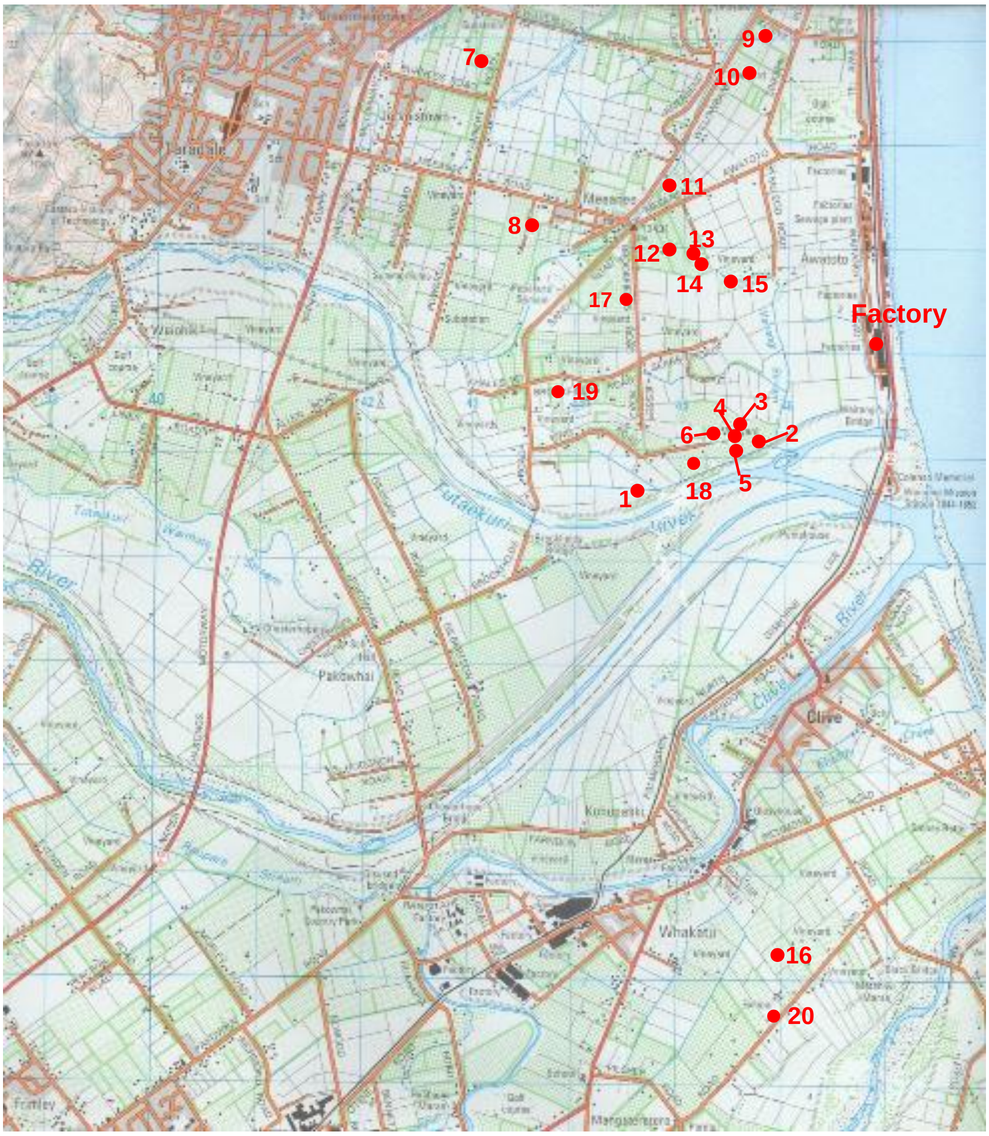

Figure 7. Location of leaf fluoride monitoring sites. Site details are given in Table 6.

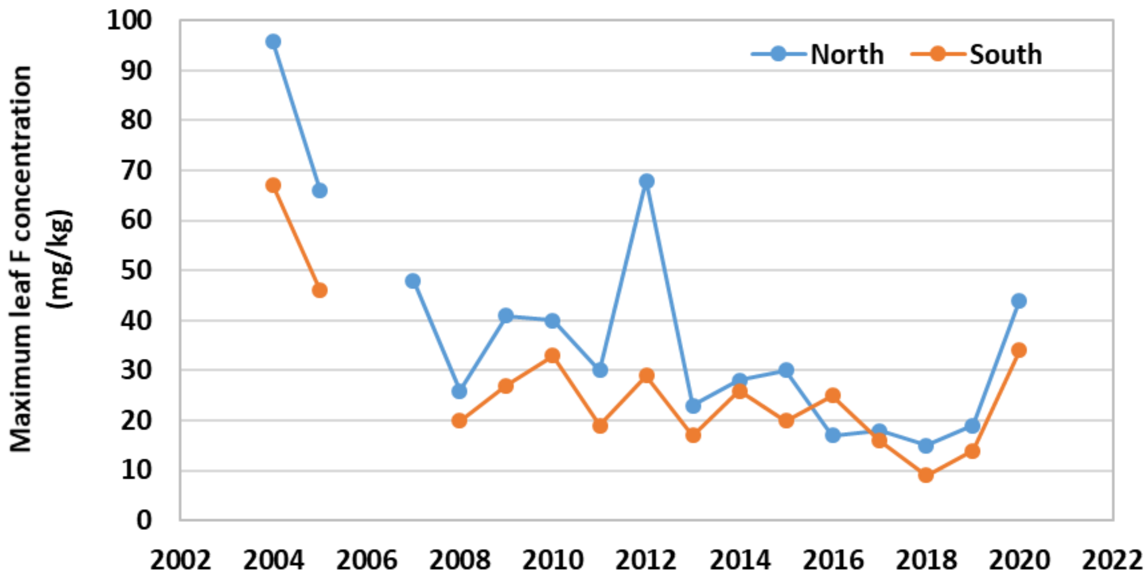

Figure 8. Maximum fluoride (F) concentrations of unwashed leaves within a given growing season recorded at sites on the northern and southern sides of Brookfields apple orchard. Data from 2004 are from Tate (2005), 2005 data from Trail et al. (2006), and the remaining data correspond to Sites 4 and 5 from monitoring by Plant & Food Research. Note that the points are plotted against the year the growing season started, e.g. data for the 2004–05 growing season are plotted against the year 2004.

Historically, the monitored site where the maximum leaf F concentration was commonly measured in a given season was Brookfields orchard, which is located at the eastern end of King Road (Sites 2–6, Figure 7). Brookfields orchard is located closer to the stack than the other sites (Figure 7) and receives more wind from the direction of the stack than sites located northwest or south of the Napier Works (Chilton 2021). Long-term monitoring data show that the maximum leaf F concentrations measured at Sites 4 and 5 have generally declined since the 2004–05 season (Figure 8). Damage attributed to F was observed at this orchard prior to the current resource consent being granted (Doley 2005), but since 2007 there has been no damage attributable to F observed at this site, or any of the other sites monitored by Plant & Food Research (Searle et al. 2009, 2011, Trolove et al. 2011, 2012, 2013, 2014, 2015, 2016, 2017, 2018, 2019, 2020). From 2007 onwards, leaf F concentrations have been <49 mg/kg, with the exception of a spike of 68 mg/kg during the 2012–13 season at the northern site (Site 4). All leaf concentrations from 2007 onwards have been below 80 mg/kg, suggesting that yield loss is unlikely to have occurred since that time, even in a F-sensitive crop such as grapes, since yield reductions have not been observed in grapes with leaf concentrations <80 mg/kg (Leece & Scheltema 1983).

The leaf F concentration data show a marked increase in seasonal maximum leaf F concentrations in sites closer than 2 km to the Napier Works (Figure 9). Prior to 2007, much higher leaf F concentrations were measured, and noticeable increases in leaf F were observed in sites 7 km from the Napier Works (Tate 2003; Doley 2005). The data collected from 2007 onwards (Figure 9) show an exponential decay in seasonal maximum leaf F concentration with increasing distance of sites from the Napier Works. It should be noted that there are no perennial horticultural crops closer to the Napier Works than approximately 1.5[2] km. Figure 9 also shows that leaf F concentrations never exceeded 20 mg/kg at sites further than 2 km from the Napier Works during the data collection period (2008–09 season to

[2] The closest perennial crops are apple orchards, which are tolerant to F. The closest F-sensitive perennial crops are located 1.9 km from the Manufacturing Stack (see Figure 6).

2019–20 season). Foliar concentrations of <20 mg F/kg in grape and apple leaves are considered to be below the threshold at which damage may occur (Trolove et al. 2020). Doley (2006b) considered that <10 mg/kg is within the normal range. Minimal F toxicity symptoms (<10% of leaf area) were observed in washed leaves from sensitive native Australian species when leaf F concentrations were below 20 mg/kg (Mitchell et al. 1981). Note that this minimum critical limit of 20 mg/kg above which leaf damage might be observed in sensitive varieties is much lower than the 80 mg F/kg limit above which economic yield loss might be observed in grapes, since plants can sustain some leaf damage without yield being affected.

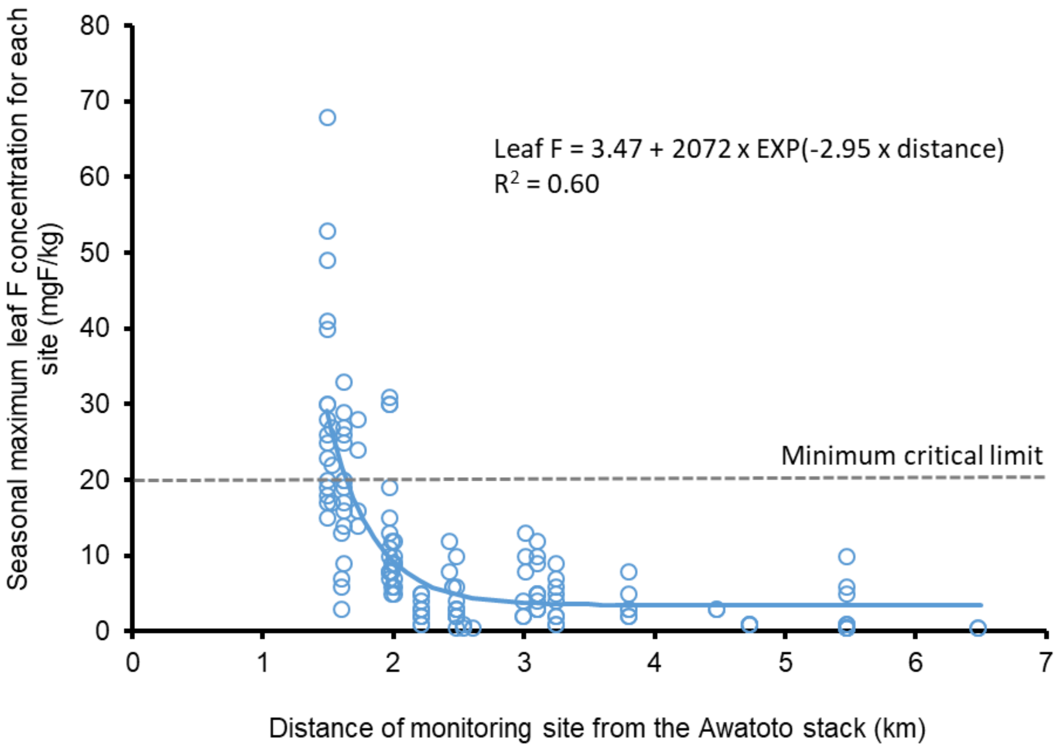

Figure 9. Plot of season maximum leaf fluoride (F) concentration for a monitoring site versus distance of the site from the Napier Works' Stack. Data are for all sites monitored by Plant & Food Research (Table 6) from the 2008–09 season until 2020–21. A minimum critical limit is shown, above which visible leaf symptoms might occur in sensitive varieties (for explanation, see footnote[3]).

Simply plotting maximum leaf F concentration versus distance is an oversimplification, since the distribution of atmospheric F around the Napier Works varies in three dimensions rather than just with linear distance, and is affected by other factors, such as the prevailing wind. A clearer (two-dimensional) picture of the effect of atmospheric F concentrations (Figure 10) is gained by plotting the average seasonal maximum leaf F concentrations onto the map of modelled atmospheric

[3] Leaf F concentrations are not an accurate indicator of the likelihood of plant damage or yield loss (Doley 2006a), rather they are one indicator of whether F is likely to be the cause of the observed damage. There are many factors that influence whether a certain leaf F concentration will cause damage, e.g. the species and variety of plant (Trolove et al. 2020), leaf age and whether the leaf samples were washed or unwashed. The minimum critical limit of 20 mg F/kg has been conservatively set, meaning that leaf damage is unlikely to be seen in plants with leaf F concentrations below this limit, but leaf damage may not necessarily be observed in plants with leaf F concentrations many times over this limit. Hence leaf samples have returned concentrations of >20 mg/kg in the monitoring programme (e.g. Figures 9 and 10), but no toxicity symptoms have been observed.

F concentrations produced by Chilton (2021). Figure 10 shows that leaf F concentrations tended to be higher to the southwest of the Napier Works, which agrees with the modelling of Chilton (2020), where atmospheric F concentrations tend to be higher in this direction than other on-land areas, since the prevailing wind blows towards the south-west (Chilton 2020). For grape vines, similar correspondence between ambient and leaf F concentrations was found in a long-term study of vineyards in the Hunter Valley, Australia (Doley & McNaughton 2014). This similarity gives a degree of confidence in the modelling of Chilton (2021), and in the leaf sampling protocol. In general, grape vines and Italian alders tend to have higher leaf F concentrations than the apples and stonefruit, for a given predicted atmospheric F concentration (Figure 10). This may be because of differences in waxiness, leaf architecture and canopy structure (Davison 1983). It can also be attributed to micro-location conditions, e.g. the difference between the stonefruit and Italian alders on Dewar’s orchard was probably because the alders acted as a shelterbelt for the stonefruit.

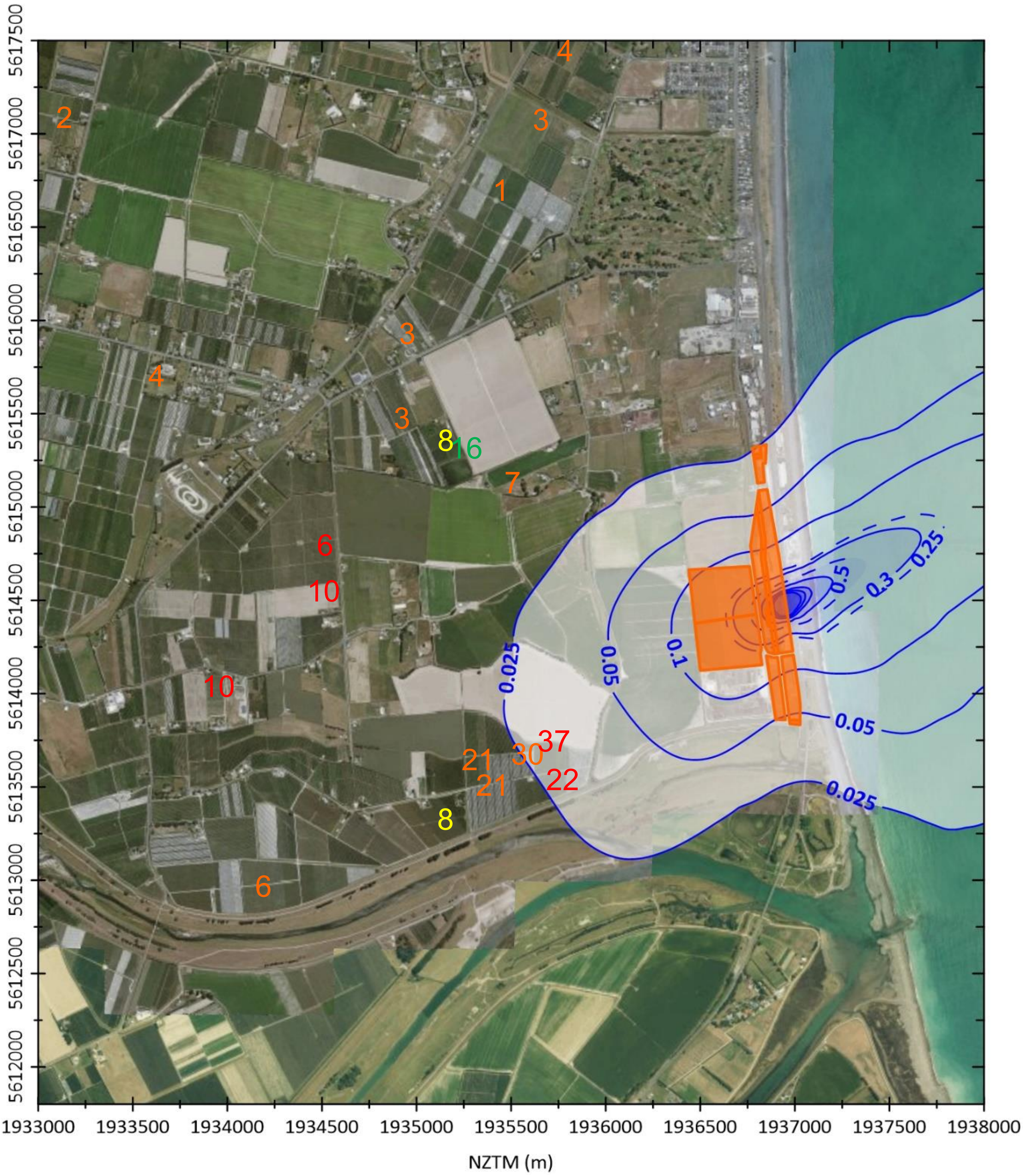

Figure 10. Average seasonal maximum F concentrations of unwashed leaves overlaid onto the modelled 90-day average atmospheric fluoride (F) concentrations for the existing stack configuration (Chilton 2021). The model assumed the Napier Works was emitting F at the 75th percentile of measured emission rates. Leaf F concentrations are averages of ≤11 seasons of data (2008/09 to 2019/20). Note that some data are averages of different seasons to other data. Numbers in blue are atmospheric F concentrations (µg/m^3), other colours are leaf F concentrations (mg F/kg leaf dry matter) of the following species: orange=apple, yellow=stonefruit, red=grapes, green=Italian alder. Ravensdown-owned land is shaded orange.

3.3.6 Effects of fluoride on pasture and annual crop species

Pasture and crop species are generally more tolerant to F and acidity than more sensitive woody species such as stonefruit and grapes (Table 4). Geelen (2006b) sprayed sweetcorn and pea seedlings, a monocotyledon and a dicotyledon species, with two different solutions of undiluted condensate from the Napier Works' stack, one at pH 2.6 and the other pH 4.5, and both had a F concentration of approximately 115 mg/L. Both species showed no visible signs of damage, indicating that these crop species are relatively resistant to harm from a single spray.

A pot experiment by Searle et al. (2007b) was established to investigate whether emissions from the Napier Works, sea spray, or some soil factor was the cause of the "Meeanee effect" – where yields in Meeanee tended to be lower than other areas of Hawke's Bay. Maize was grown in soil from Meeanee and compared with growth in soil from the [then] Crop & Food Research site at 265 Lawn Road, Mangateretere. The experiment was conducted in a greenhouse at the [then] Crop & Food Research site. At the two-leaf stage the maize was sprayed with either distilled water, condensed stack liquor from the Napier Works (pH 2.7, 34 mg F/L), sea water, or a 1:1 mix of sea water and stack liquor. The results showed that none of the treatments affected the growth of the plants. There was slight chlorotic stippling on a proportion of the plants that were sprayed with seawater, with 48% expressing foliar damage for those receiving pure seawater, and 38% for the 1:1 mix of seawater and liquor. This was significantly greater than plants that received straight liquor (4% damage) or the distilled water controls (0% damage). The authors concluded that stack liquor had no noticeable effect on maize growth in this experiment.

3.3.7 Effects of fluoride on ornamental and native plants

A number of ornamental or fruit species that are commonly planted in gardens in Hawke's Bay are classified as 'sensitive' to F. This includes flowering bulbs such as Crocus, Freesia, Iris, hyacinth and tulip, with *Gladiolus* identified as being *'very sensitive'* to F *(*Doley et al. 2004*). 'Fluoride-sensitive'* shrubs include Azalea, Hydrangea, Protea, some bottlebrushes, guava, blueberry and stonefruit; and trees such as cedar, blackwood, some wattles, sycamore and some maples, some *Eucalyptus* spp., ash, some palms and some spruce species (Doley et al. 2004; Davison 2005). A number of native species are also 'sensitive' to F, including cabbage trees, the native flax (harakeke), tarata (lemonwood), totara and lancewood (Doley et al. 2004). Cabbage trees and the native flax are currently growing in the Waitangi Regional Park near the Napier Works, and the other native species may be grown in gardens in the Awatoto area. Note that of the 46 native New Zealand species listed by Doley et al. (2004), none were identified as being 'very sensitive' to F. To our knowledge there have been no complaints of damage to ornamental or native plants made to the HBRC or Ravensdown since 2008. The only exception to this was an allegation of damage to some garden species at Plumpton Park in 2018. This was investigated by Plant and Food Research and concluded that the damage was unlikely to be caused by the Napier Works, and more likely attributed to salt-laden winds (Section 4 and Appendix 1b). A visual assessment of the cabbage trees and flax growing in the Waitangi Regional Park during July 2020 and in August and September 2021 showed no evidence of F damage (see Appendix 2).

3.3.8 Assessment of atmospheric modelling results

The amount of F emitted has declined considerably since the reports of F damage to crops in the 2002/03 and 2003/04 seasons. During these seasons the average F emission rates (30 data points per average) were between 2.5 and 23 kg/h (Trail et al. 2005). Since the upgrading of the pumps in the venturi pipes in early 2004, this average dropped to 1 kg/h, or less (Trail et al. 2005). Over the last 6 years (2011–12 to 2019–20), the hourly F emission rate has been 0.07 kg/h (Chilton 2021).

Atmospheric F concentrations in the air surrounding the Napier Works, based on the existing stack arrangement, and assuming Ravensdown are emitting F at the 75th percentile of measured values for 90 days, have been modelled by Chilton (2021). The trends from this modelling (Figure 11) show greater F concentrations to the southwest of the Napier Works, which agrees with the distribution of average maximum leaf F concentrations measured in leaves from orchards located around the Awatoto–Meeanee area (Figure 10). This provides some confidence that the trends shown by the modelling are realistic. This modelling (Chilton 2021) shows that if Ravensdown emits F at above-average concentrations for long periods, that the atmospheric F concentrations will remain below those that are likely to cause economic damage to crops surrounding the Napier Works. As a specific example, atmospheric F concentrations generated by Ravensdown emitting F at the 75th percentile of measured values for 90 days, are not predicted to exceed the critical concentration of 0.25 µg F/m^3 for the most F-sensitive crops (classified as Special Land-Use, Table 3) on any agricultural land outside of the Ravensdown boundary (Figure 11).

With the current distribution of crops, the practice of low F emissions from the Napier Works since 2004, and adjusting the pH of the stack emissions, there have been no reported instances of crop damage attributable to emissions from the Napier Works since these changes were implemented (Section 3.4).

Worst-case scenario modelling of short-term emissions (12 h, 24 h and 7 d) was conducted by Chilton (2021). This assumed that Ravensdown emitted F at the maximum rate proposed in their Air Discharge Strategy of 1.0 kg F/h, which is highly unlikely from a plant operations perspective (Andrew Torrens, Ravensdown, pers. comm.), given that their current average is 0.07 kg/h (Chilton 2021). This worst case modelling predicts that atmospheric F concentrations will not exceed the critical concentration for General Land-Use beyond its boundaries (except to the east of the Napier Works, where no agricultural land exists, Figure 12). The land immediately northwest and west of the Napier Works is in pasture, which is tolerant of F (Table 4), and there have been no reports of damage. Fluoride-sensitive crops are located 1.9 km from the Napier Works (Figure 6), so should not experience economic yield loss from F, since concentrations that exceed those specified for the Special Land-Use category extend up to ~1.0 km from the Napier Works' Manufacturing Stack in the 12 h modelling scenario (Figure 12). Note that if a F-sensitive crop was established within ~1.0 km of the Napier Works' Manufacturing Stacks, and Ravensdown emitted F at the maximum allowable rate for 12 h, then the modelling suggests that the F limits for Special Land-Use would be exceeded and loss of economic yield might occur. This being said, the current leasee of the site has grown many crops of maize, which is classified as being sensitive–intermediate to F (Table 4), on the paddock immediately west of the Ravensdown boundary, and within 1 km of the Napier Works. There have been no reports of damage. In 2014, the maize grain yield was 14 t/ha (Kieran Murray, pers. comm.), which is above the New Zealand average of 11 t/ha (AIMI 2019).

The modelling of Chilton (2021), based on the proposed Air Discharge Strategy, suggests that atmospheric F concentrations over the Waitangi Regional Park should not reach the critical concentration for General Land-Use (Figure 12), which was recommended as appropriate for coastal species (Doley 2020). The highest F concentration modelled was for the 12-h scenario, where concentrations exceeded the Special Land-Use limit of 1.8 µg/m^3 in the northern edge of the park if Ravensdown emits F at the maximum permissible rate for a period of 12 h (Figure 12A). This area is currently in pasture, which is tolerant of F (Table 4), so these concentrations are not a cause for concern. Some F-sensitive species have been planted in the Waitangi Regional Park, such as tarata (lemonwood), harakeke (native flax) and cabbage trees (Appendix 2); however, these have not been planted along the northern boundary of the Park, which is predicted to have F concentrations that exceed those for Special Land-Use under the worst-case scenario modelled in Figure 12A.

The risk of any damage from F will be further reduced since Ravensdown propose to modify their Manufacturing Stacks, which includes combining all three into one system and increasing the stack height to 50 m. Atmospheric modelling of the effects of these changes by Chilton (2021) indicates that F concentrations at ground level, and consequentially the acidity associated with that F, in the area surrounding the Napier Works will decrease slightly (Figure 11). One question that has been raised is "Since the stack emissions are released higher into the atmosphere, this reduces pollutant concentrations close to the stack, but does this increase the risk of damage to vegetation further away?" The short answer to this question is "No", because as the emissions travel further from the stack they disperse, which reduces the concentration. This is illustrated in the modelling of Chilton (2021), where the maps of modelled atmospheric F concentrations around the proposed higher stack show slightly lower concentrations at all distances from the stack than the current stack arrangement (Figure 11). So, while pollutants are more likely to be deposited further away from the stack if the height is increased, they will be deposited at concentrations well below established critical concentrations. Therefore, when the proposed Manufacturing Stack modifications proceed, this should provide a further small reduction in the risk of damage from F or acidic emissions (Trolove 2020).

3.3.9 Are fluoride emissions from the Napier Works a cause for concern?

The atmospheric modelling at the maximum permissible rate, leaf sampling, site monitoring and complaints investigations all indicate that F emissions to air from the Napier Works have not been a cause for concern to the vegetation surrounding the Napier Works since the current resource consent was granted, given the current distribution of crop species. Atmospheric modelling of the worst-case scenario indicates that F emissions may be a cause for concern if F-sensitive species are planted closer than 1.0 km to the Napier Works’ Manufacturing Stack, and Ravensdown emit F at the maximum rate of 1.0 kg/h for approximately 12 h or more, which is highly unlikely.

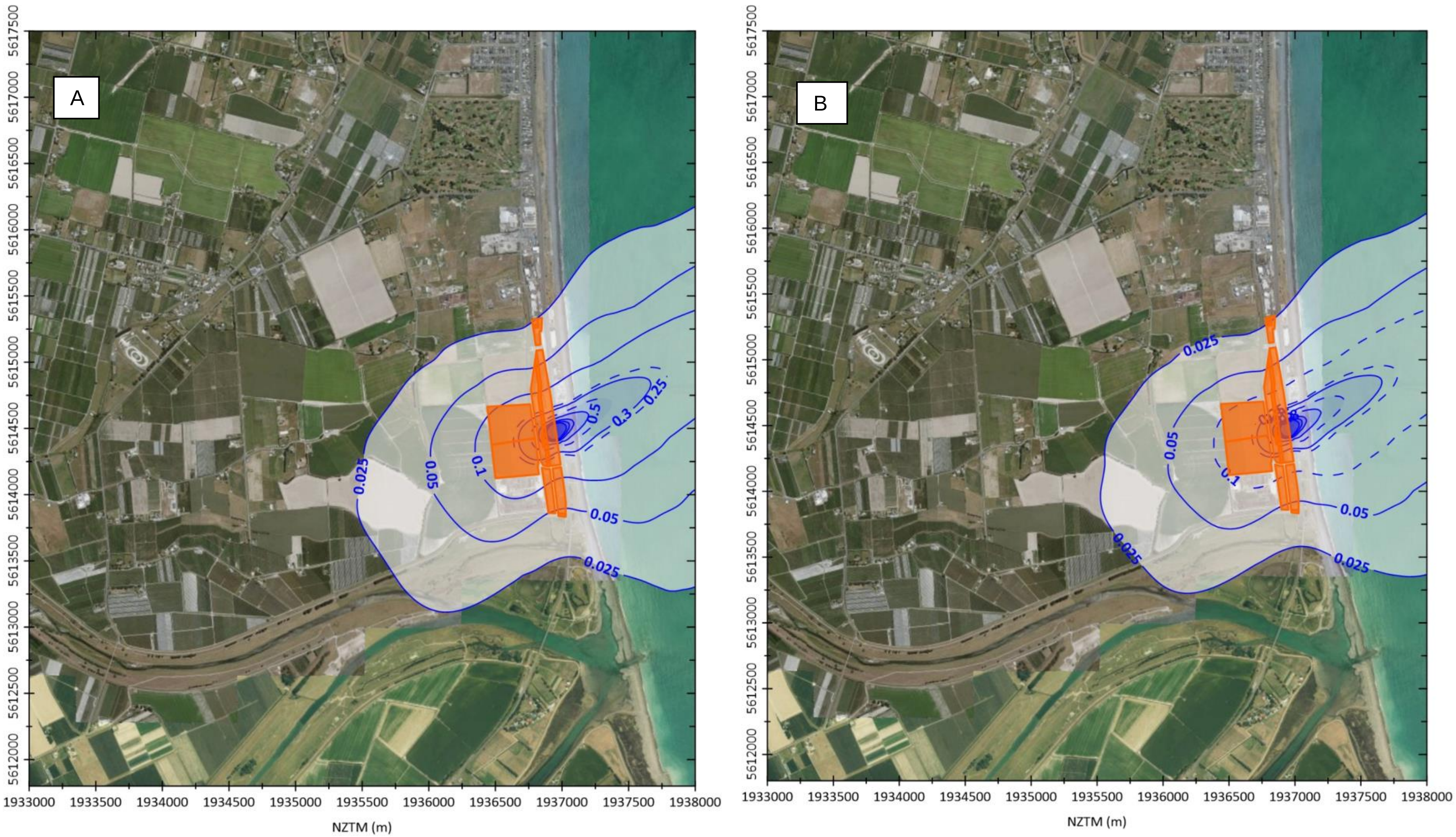

Figure 11. Modelled 90-day average atmospheric fluoride (F) concentrations (µg/m^3) at ground level around the Napier Works for the existing (A) and proposed (B) 50-m stack scenarios. Ravensdown-owned land is shaded orange. The model assumed the Napier Works was emitting F at the 75th percentile of measured manufacturing rates. Source: Chilton (2021).

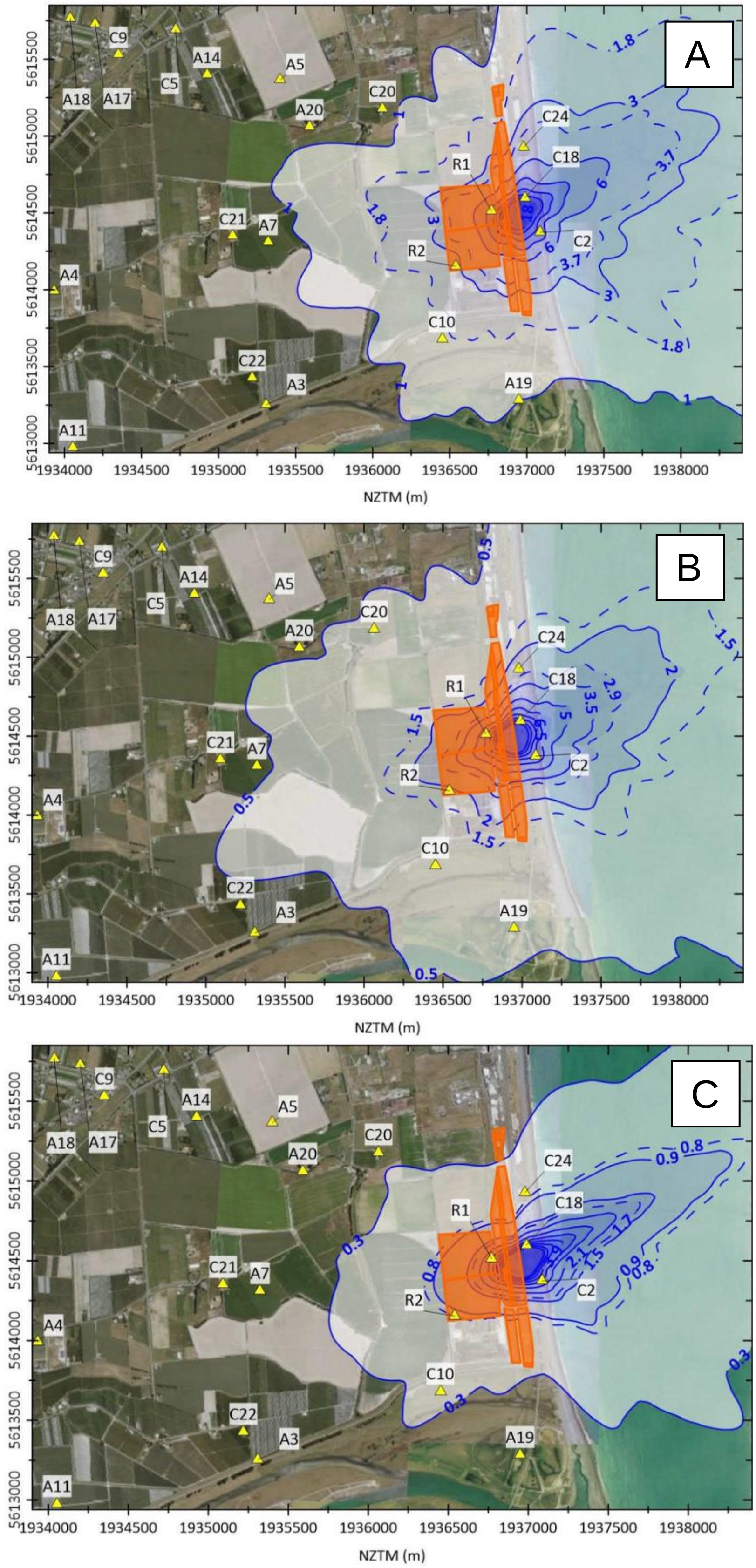

Figure 12. Predicted maximum 12-h (A), 24-h (B) and 7-day (C) average atmospheric fluoride concentrations (µg/m³) at ground level – based on a peak emission rate of 1.0 kg F/h as outlined in the proposed Air Discharge Strategy. Critical concentrations for General Land-Use and Special Land-Use are shown as dashed lines (see Table 3). Source: Chilton (2021). Critical concentrations for General Land-Use for figures A, B and C are 3.7, 2.9 and 1.7 µg/m^3, respectively. Critical concentrations for Special Land-Use for figures A, B and C are 1.8, 1.5 and 0.8 µg/m^3, respectively

3.4 Dust

3.4.1 Effects on vegetation

Possible effects of high concentrations of dust on vegetation include: an increase in water loss, blocked stomata, an increase in leaf temperature and a decrease in photosynthesis (Farmer 1993). The one study that investigated the effects of dust from a fertiliser factory examined the growth of Scots pine, and found an increase in growth in younger trees (perhaps from nutrients in the fertiliser) and a decrease in growth and leaf damage in older trees (Farmer 1993).

3.4.2 Are dust emissions from the Napier Works a cause for concern?

The Resource Management Act sets limits for dust particles (PM_{10}, particulate matter ≤10 µm in diameter) that may affect human health and the environment of 50 µg/m^3 averaged over a 24-h period. PM_{10} concentrations coming from the Napier Works were modelled by Chilton (2021) and were well below the 50 µg/m^3 critical limit (Figure 13). There have been no cases of complaints of dust affecting vegetation made to Plant & Food Research or Ravensdown. Dust emissions are not considered a cause for concern to vegetation.

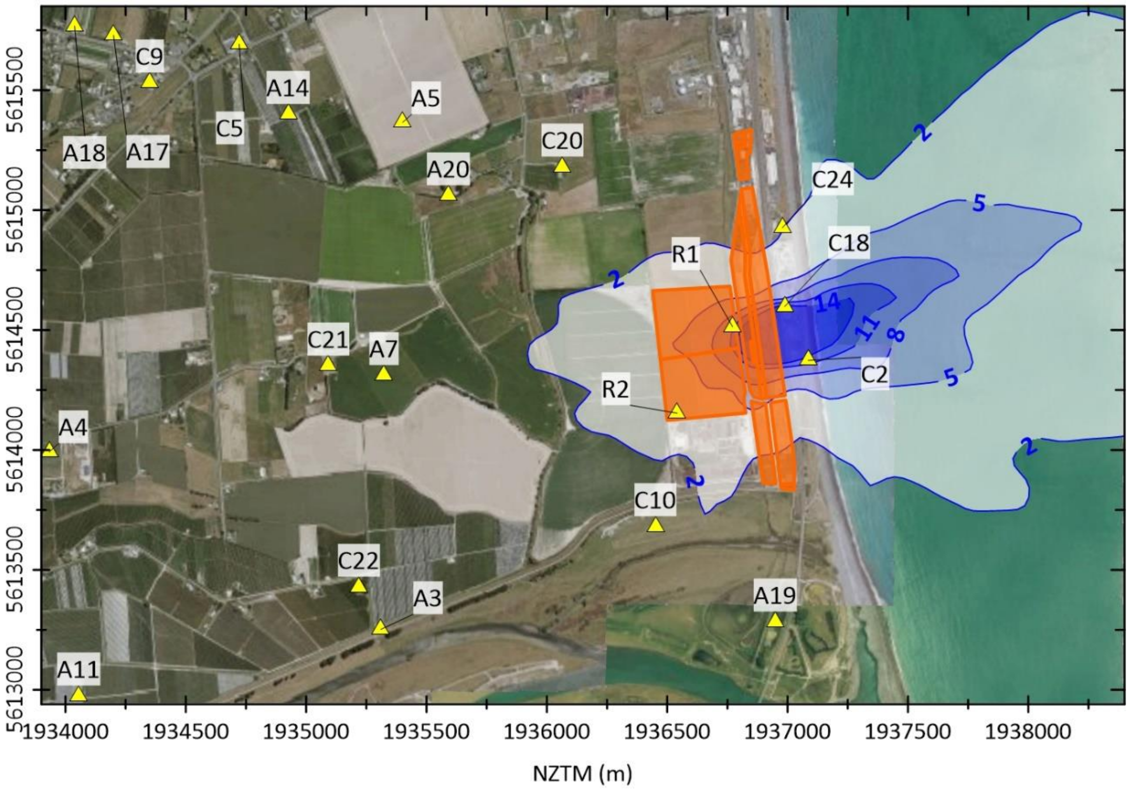

Figure 13. Predicted maximum 24-hour average particulate matter ≤10 µm in diameter (PM_{10}) ground level concentrations (µg/m³) in the immediate surroundings – based on peak emission rates. Site emissions only. Source: Chilton (2021).

4 Incident investigations

In his statement of evidence to the HBRC in December 2006, Dr David Doley stated *that "In my opinion, it has not been possible to link in a scientifically defensible way the Awatoto Works with any occurrences of injury to crop or ornamental species after emission limiting procedures were instituted by Ravensdown. The primary reason for this view is the absence of reports of injury to crop species in late summer of 2006 or during the period of spring growth in 2006"* (Doley 2006a, paragraph 1.9). Since spring 2006, there have been allegations of damage to crops and ornamental species; each allegation was carefully investigated, and none of these investigations concluded that it was likely that the damage was a consequence of emissions from the Napier Works (Searle 2007, 2008a,b; Appendix 1a,b). A brief summary of these allegations, that Ravensdown, Plant & Food Research and HBRC are aware of, since the current resource consent was issued in March 2007, is provided in Table 7. The investigations found that the observed damage was most likely caused by salt-laden winds, nutrient imbalances, plant pathogens or waterlogging.

The number of complaints decreased dramatically after 2008. Detailed reports of the only two complaints since the pH of the Manufacturing Stack was increased to ≥2.7 in 2008, are provided in Appendix 1. In brief, for both of these complaints, plant tissue F concentrations were low. For the first complaint, the observed damage was probably lenticel breakdown caused by low calcium; and for the second complaint, leaf samples showed high leaf sodium and the symptoms were consistent with damage from salt-laden wind.

Table 7. List of complaints alleging that the Napier Works may have caused crop injury, and the findings of the investigations, since the current consent was issued on 22 March 2007.

Incident No.	Date	Location	Species	Nature of complaint	Finding	Leaf F (mg/kg)	Reference
001/18	Jan 2018	Plumpton Park	Black walnut Apple Cherry	Necrotic areas, mainly on the edges of apple and walnut leaves. Bronzing on the underside of apple leaves. Slightly rolled leaves in apple and cherry	Necrosis likely due to salt-laden wind. Leaf rolling commonly observed in cherries grown well away from the Napier Works	Apples: <1 in both affected and unaffected Walnut: 7 in affected, 5 in unaffected	Trolove & Sorensen (2018), see also Appendix 1a
001/16	Apr 2016	B Dewar's property, 39 Awatoto Rd	'Fuji' apple	Browning around blackened lenticels on apple fruit. Symptoms were worse on the side facing the sun	Lenticel breakdown (or possibly lenticel blotch pit) resulting from nutrient imbalance	F <1 in skin from affected and unaffected apples	Trolove S, pers. comm., 25 May 2016, see also Appendix 1b
002/08	Feb 2008	B Dewar's property, 39 Awatoto Rd	Italian alder	Die-back from outer margins of individual leaves	Damage suggested to be caused by salt-laden sea breeze	13 in affected leaves, 3 in unaffected leaves	Searle (2008b)
001/08	Jan 2008	B Dewar's property, 39 Awatoto Rd	'Fuji' apple and plum	Apples – paleness/yellowing of foliage at the top of trees. General leaf necrosis/spotting in the mid-lower canopy. Plums – extensive burning and loss of leaves at the top of trees. General leaf necrosis/spotting in the mid-lower canopy	Apples: ● leaf yellowing: Nutrient stress ● leaf browning: Mg deficiency ● leaf blotching: Fungal disease Plums: ● leaf burning: Nutrient stress ● leaf chlorosis: Nutrient stress ● leaf blotching: Tatter leaf or false shot hole disease	Apples: 4–7 in affected, 3–4 in unaffected Plum: 2–4 in affected, 3–4 in unaffected	Searle (2008a)
17040701	Apr 2007	B Dewar's property, 95 McLeod Rd	Italian alder	Leaf margins and tips show browning and drying of tissue. Young leaves mainly affected	High leaf Cl concentrations. Damage attributed to high water table	9.7 in affected leaves, 9.5 in unaffected	Searle (2007)
19030701	Mar 2007	B Dewar's property, 95 McLeod Rd	Italian alder	Leaf margins and tips show browning and drying of tissue. Young leaves mainly affected	High leaf Cl concentrations. Damage attributed to high water table	6.7 in affected leaves, 4.7 in unaffected	Searle (2007)
19030702	Mar 2007	B Dewar's property, 39 Awatoto Rd	Kiwifruit vines	Small leaves and poor canopy growth	Waterlogging	4 in affected	Searle (2007)

5 General conclusions

- There were reports of damage to vegetation by F emissions to air prior to Ravensdown lowering their F emission rate to <1.5 kg/h in 2005, and by acidic emissions prior to Ravensdown adjusting the pH of stack emissions to >2.7 in 2008. Since those adjustments have been made, there has been no evidence of damage to vegetation that would likely be attributable to emissions from the Napier Works. All the complaints since 2008 were investigated by Plant & Food Research and the damage observed is likely the result of other causes, e.g. salt-wind damage or low calcium.

- Atmospheric modelling indicates that the risk of future damage from F or SO_2 is minimal, since conservative modelling indicates that the concentrations of these pollutants are below MfE critical values.

- A literature review indicated that a pH of >2.7 for stack emissions should be generally appropriate to avoid damage to vegetation and fruit by acidic aerosols. However, the review did suggest there is a low possible risk that some damage may arise from regular, intermittent exposure to acidic emissions of pH ≤4.0, depending on the crop species and growth stage, particularly under misty or highly humid conditions without significant rainfall (≤0.2 mm).

- The literature review also identified that there may be a reduction in pollination or fruitset upon exposure to emissions of pH <2.75–4.7 (depending on crop species and variety), but that this does not necessarily result in a loss of yield.

- The fact that damage has not been documented to occur during the current resource-consent period suggests that the risk of damage from acidic aerosols is low.

- Dust emissions are not considered a cause for concern for vegetation outside of Ravensdown's boundary.

6 Recommendations

Ravensdown should be aware of the F-sensitivity of crop species planted within 1.0 km of the Napier Works. The low risk of any F damage to any sensitive species will be avoided by:

- Reducing fugitive emissions via the proposed Source Control Plan.
- Avoiding extreme operating conditions, since normal factory operations release F at much lower rates (an average of 0.07 kg/h) than the 1.0 kg/h rate for 12 h used in the model.
- The very low risk of damage from acidic aerosols at pH <4.0 with repeated exposure could be mitigated by adjusting the Manufacturing Stack emissions to pH >4.0 under misty or very humid conditions where the wind was blowing towards an orchard for a period greater than 30 minutes. These weather conditions are described in condition 39 of the current consent: i.e. the pH should be adjusted to >4.0 when the wind speed is <3 m/s and the wind direction is between 030° and 155° (i.e. on-shore) and the temperature is >22°C, it is dark and the relative humidity is >70%.
- This condition would only hold during the growing season for pipfruit and stonefruit (late August to end of April). For the growing season outside of the flowering period (i.e. for the months of November to April) the risk is only for multiple exposures, so emission pH of <4.0 on up to 3 different days should not be considered a breach of resource consent. This condition is conservative and based on pH data only; it should be reviewed if information is found that allows the risk of acid damage to be modelled, and if the risk is found to be negligible.
- A visit to the Waitangi Regional Park should be included in the regular monitoring of vegetation sites. This could involve a visual assessment for any signs of vegetation damage that may possibly be, or appear to be, from emissions by the Napier Works. Leaf sampling of affected and unaffected leaves could be conducted if any symptoms were observed. This site visit could be in place of Brookfields monitoring site 5 (Table 6 and Figure 7), which usually has very similar, but slightly lower, leaf F concentrations to Brookfields site 4 (Trolove et al. 2011, 2012, 2013, 2014, 2015, 2016, 2017, 2018, 2019, 2020).

7 Acknowledgement

The author thanks Robert Ward for producing the map from the land cover database.

8 References

AIMI 2019. New Zealand survey of maize areas and volumes: June 1, 2019. Arable Industry Marketing Initiative. FAR Saville Stat. https://www.far.org.nz/assets/files/blog/files/329b6cfa-cc0c-5290-b186-ead1c5c8c1bc.pdf [accessed 8 October 2021].

Ashenden TW, Bell SA 1987. The effects of simulated acid rain of the growth of three herbaceous species grown on a range of British soils. Environ Pollut 48: 295-310.

Ashenden TW, Rafarel RF, Bell SA 1991. Exposure of two upland plant species to acidic fogs. Environ Pollut 74: 217-225.

AgFirst Consultants 2005. The potential impact of fluoride emissions on neighbouring horticultural crops. Report prepared for Ravensdown Fertiliser Co-operative Ltd and Glasson Potts Fowler. 23 p.

Barritt BH, Kammereck R 1983. Association of calyx green end disorder of golden delicious apples with tissue fluoride. J Am Soc Hortic Sci 108(2): 342-346.

Blakey R 2018. Managing lenticel breakdown – Don’t get caught by the snowball. Proceedings from the Empire State Producers Expo, 16-18 January 2018, Syracuse, NY.

Bressan RA, Le Cureux L, Wilson LG, Filner P. 1979. Emission of ethylene and ethane by leaf tissue exposed to injurious concentrations of sulfur dioxide or bisulfite ion. Plant Physiol 63: 924-930.

Buse-Dragomir L 2010. Researches on flourine pollution influence on the physiology of the cropped species. Ann Univ Craiova Agric Montanol Cadastre Ser 40: 75-81.

Cape JN 1993. Direct damage to vegetation caused by acid rain and polluted cloud: definition of critical levels for forest trees. Environ Pollut 82: 167-180.

Chemetics® 2021. Emissions reconsenting report: Ravensdown Limited, Napier, New Zealand. Chemetics Project No. 217073-35836. Issue C. Final Issue September 15, 2021.

Chilton R 2021. Reconsenting of Ravensdown Napier Works: Air Quality Assessment. Version 5. Report prepared for Ravensdown Ltd. Job No. 1012315. Tonkin & Taylor Ltd. 121 p.

Choi EY, Moon JH, Lee WM, Son SH, Lee SG, Cho IH. 2010. The response of antioxidant enzyme activity, growth and yield of pepper and watermelon plants to a single application of simulated acid rain. J Food Agric Environ 8: 1265-1271.

Cox RM. 1984. Sensitivity of forest plant reproduction to long range transported air pollutants: *in vitro* and *in vivo* sensitivity of *Oenothera parviflora* L. pollen to simulated acid rain. New Phytol 97: 63-70.

Davison A 1983. Uptake, transport and accumulation of soil and airborne fluorides by vegetation. In: Shupe JL, Peterson HB, Leone NC, eds. Fluorides: effects on vegetation, animals and humans. Salt Lake City, UT, Paragon Press. Pp. 61-82.

Davison A 2005. Air pollution effects on plants. University of Newcastle upon Tyne www.ncl.ac.uk/airweb/fluoride/tables.htm [accessed by Wayback Machine 31 July 2020].

Dinh DL, Buchloh G, Oelschlager W 1973. Auswirkung von Fluorverbindungen auf die Pollenkeimung und den Fruchtansatz von Obstgewachsen. Erwerbsobstbau 15: 154-157.

Doley D 1986. Plant-Fluoride Relationships. Inkata Press, Melbourne.

Doley D, McNaughton K, Wenta P 2003. Aluminium production in the Hunter Valley environment: vineyards. Proceedings of the National Conference of the Clean Air Society of Australia and New Zealand, Newcastle. Clean Air Society of Australia and New Zealand, Eastwood. 6 p.

Doley D, Hill RJ, Riese RH 2004. Environmental fluoride in Australasia: ecological effects, regulation and management. Clean Air Environ Qual 38: 35-55.

Doley D 2005. Effects of atmospheric emissions on horticultural crops in the Awatoto area. A review for Ravensdown Fertiliser Co-operative Ltd. Indooroopilly, Qld, Australia.

Doley D 2006a. Statement of Evidence. Before the Hawke's Bay Regional Council in the matter of the Resource Management Act 1991 and in the matter of an application by Ravensdown Fertiliser Co-operative Limited for resource consent (DP0500561A).

Doley D 2006b. Analysis of injury to horticultural crops in the Awatoto area, 2005-2006 growing season. Indooroopilly, Qld, Australia.

Doley D 2008. Analysis of environmental conditions potentially associated with injury to horticultural crops in the Awatoto-Meeanee area. Indooroopilly, Qld, Australia.

Doley D, McNaughton K 2014. Vineyard monitoring of fluoride in the Hunter Valley during and after an aluminium smelter operation. Air Qual Clim Change 48 (2): 25-34.

Doley D 2020. Statement on Environmental Conditions in the Vicinity of Ravensdown Awatoto Works. 3 July 2020.

Edmunds GF 1983. Effects of fluoride on plant-insect interactions. In: Shupe JL, Peterson HB, Leone NC, eds. Fluorides: effects on vegetation, animals and humans. Salt Lake City, UT, Paragon Press. Pp. 151-156.

Farmer AM 1993. The effects of dust on vegetation – a review. Environmental Pollution 79: 63-75.

Forsline PL, Musselman RC, Dee RJ, Kender WJ 1983a. Effects of acid rain on grapevines. Am J Enol Vitic 34: 17-22.

Forsline PL, Musselman RC, Kender WJ, Dee RJ 1983b. Effects of acid rain on apple tree productivity and fruit quality. J Am Soc Hort Sci 108: 70-74.

Fowler D, Cape JN, Deans JD, Leith ID, Murray MB, Smith RI, Sheppard LJ, Unsworth MH 1989. Effects of acid mist on the frost hardiness of red spruce seedlings. New Phytol 113: 321-335.

Fowler D, Morse AP, Gallagher MW, Choularton TW 1990. Measurements of cloud water deposition on vegetation using a lysimeter and a flux gradient technique. Tellus 42B: 285-293.

Geelen JAR 2006a. An evaluation of apple fruit and foliage tolerance to Ravensdown stack condensate. Havelock North, J.A.R. Geelen Research Ltd. 19 p.

Geelen JAR 2006b. An evaluation of pea and corn tolerance to two Ravensdown stack condensates. Havelock North, J.A.R. Geelen Research Ltd. 35 p.

Haber MF, Young E, Faust M 1983. Effects of PEG-induced water stress on calcium uptake in peach seedlings. J Am Soc Hortic Sci 108: 737-740.

Horntvedt R 1988. The effect of acid precipitation on epicuticular wax in Norway spruce and lodgepole pine. Meddelser Norsk Institutt for Skogforskning 40: 1-13.

Jacobson JS, Bethard T, Heller LI, Lassoie JP 1990. Response of *Picea rubens* seedlings to intermittent mist varying in acidity and in concentrations of sulfur and nitrogen containing pollutants. Physiol. Plant 78: 595-601.

Jacobson JS 1991. The effects of acid precipitation on crops. In: Chadwick MJ, Hutton M. Acid Depositions in Europe. York, NY, Stockholm Environment Institute. Pp. 81-98.

Kelly F 2021. Environmental Health Effects Assessment: Reconsenting of Ravensdown Napier Works. Environmental Medicine Limited.

Kingett Mitchell Limited 2005. Assessment of air emissions, superphosphate manufacturing, Ravensdown, Napier. Report prepared for Ravensdown Fertiliser Co-operative.

Klemm O 1989. Acid neutralizing of leaf surfaces: A call for a standard unit. Environ Expt Bot 30: 35-41.

Klymenko OE, Klymenko MI 2003. Acid precipitation and peach tree growth. In: Balder H, Strauch KH, Backhaus GF, eds. Second International Symposium on plant health in urban horticulture, Berlin, Germany, 27-29 August, 2003. Pp. 190-192.

Laurance JA 1983. Effects of fluoride on plant-pathogen interactions. In: Shupe JL, Peterson HB, Leone NC, eds. Fluorides: effects on vegetation, animals and humans. Salt Lake City, UT, Paragon Press, Pp. 145-150.

Laurence JA, Kohut RJ, Amundson RG 1989. Response of red spruce seedlings exposed to ozone and simulated acidic precipitation in the field. Arch Environ Contam Toxicol 18: 285-290.

LCDB 2020. Land cover database version 5.0. Landcare Research New Zealand Ltd. https://lris.scinfo.org.nz/layer/104400-lcdb-v50-land-cover-database-version-50-mainland-new-zealand/ [accessed 6 July 2020].

Leece DR, Sheltema JH 1983. Effects of fluoride emissions from injury on the fluoride concentration of grape leaves (*Vitis vinifera* L.) in New South Wales. In: Shupe JL, Peterson HB, Leone NC, eds. Fluoride: Effects on vegetation, animals and humans. Salt Lake City, UT, Paragon Press.

McCool PM, Musselman RC, Sterrett JL. 1990. Injury of three ornamental flower crops from simulated acidic fog. Plant Dis 74: 310-312.

MfE 2002. Ambient Air Quality Guidelines. Air Quality Report No. 32. Wellington, Ministry for the Environment.

Mengel K, Kirkby A 2001. Principles of Plant Nutrition. 5th Edition. Kluwer Academic Publishers, Dordrecht.

Mitchell AD, Dowling BJ, Scheltema JH 1981. Effects of fluoride on Australian vegetation. Proceedings of the Seventh International Clean Air Conference of the Clean Air Society of Australia and New Zealand. Adelaide, Ann Arbor Publishers. Pp. 479-493.

Mitchell RL 1986. Evaluation of washing techniques for the removal of external fluoride from ironbark and grape leaves. J Aust Inst Agric Sci 52: 99-101.

Munzuroglu O, Obek E, Geckil H 2003. Effects of simulated acid rain on the pollen germination and pollen tube growth of apple (*Malus sylvestris* Miller cv. Golden). Acta Biol Hung 54: 95-103.

Musselman RC, McCool PM. 1994. Acid precipitation injury to azaleas. Am Rhodo Soc J 48: 12-13.

Nemeskeri E, Kovac-Nagy E, Nyeki J, Srdi E 2015. Responses of apple tree cultivars to drought: carbohydrate composition in the leaves. Turkish J Agric For 39: 949-957.

Okpodu CM, Alscher RG, Grabau EA, Cramer CL 1996. Physiological, biochemical and molecular effects of sulfur dioxide. J Plant Physiol 148: 309-316.

OMAFRA 2009. Lenticel breakdown. Ontario Ministry of Agriculture, Food and Rural Affairs. http://www.omafra.gov.on.ca/IPM/english/apples/diseases-and-disorders/lenticel-breakdown.html [accessed 25 May 2016].

Paoletti E, Bellani LM 1990. The in vitro response of pollen germination and tube length to different types of acidity. Environ Pollut 67: 279-286.

Percy K 1991. Effects of acid rain on forest vegetation: morphological and non-mensurational growth effects. In: Effects of Acid Rain on Forest Resources. Proceedings of a conference held in Ste. Foy, Quebec, Forestry Canada, Ottawa, pp. 97-110.

Phillips N, De Luca S, Stewart M 2021. Ravensdown Awatoto discharge consent – Assessment of Estuarine Ecological Effects. Report RVD2101, Streamlined Environmental, Hamilton.

Rhimi N, Ben Ahmed C, Elloumi N, Athar HR, Noreen S, Ashraf M, Ben Abdullah F, Ben Nasri-Ayachi M 2016. Morpho-anatomical and physiological changes in grapevine leaves exposed to atmospheric fluoride and sulfur dioxide pollution. Appl Ecol Environ Res 14(5): 77-89.

Rinallo C, Raddi P, Gellini R, Di Lonardo V 1986. Effects of simulated acid deposition on the suface structure of Norway spruce and silver fir needles. Eur J Forest Pathol 16: 440-446.

Rinallo C 1992. Effects of simulated acid-rain on the foliage and fruit yield of *Malus domestica* Borkh. J Hort Sci 553-559: 67.

Rinallo C, Modi G, Ena A, Calamassi R 1993. Effects of simulated acid rain on the chemical composition of apple fruit. J Hort Sci 68: 275-280.

Searle B 2007. Incident reports: Monthly summaries. Updated July 2007. Crop & Food Research Report prepared for the Vegetation Review Committee.

Searle B, Sorenson I, Rogers B, Arnold N, Johnstone P, Shaw S, Reid J 2007a. Fluoride and acidity effects on apples – an interim report. Crop & Food Research Confidential Report No. 1856.

Searle B, Johnstone P, Arnold N 2007b. Quantifying the ‘Meeanee Effect’. Crop & Food Research Confidential Report prepared for Ravensdown Fertiliser Co-operative Limited.

Searle B 2008a. Report – Incident 001/08. Crop & Food Research.

Searle B 2008b. Report – Incident 002/08. Crop & Food Research.

Searle B, Sorensen I, Shaw S, Rogers B, Arnold N, Johnstone P, Reid J 2008. Fluoride and acidity effects on apple. Crop & Food Research Confidential Report No. 2090.

Searle B, Sorensen I, Arnold N 2009. Monitoring of F and pH levels in Meeanee area for the 2008-2009 season. A report for Hawke's Bay Regional Council. Hastings, Plant & Food Research.

Searle B, Sorensen I, Trolove S, Arnold N 2011. Monitoring of leaf fluoride concentrations in the Meeanee area for 2009-10. Hastings, Plant & Food Research.

Stevenson C, Halley V, Noonan M. 2000 Effects of air contaminants on ecosystems and recommended critical levels and critical loads. Air Quality Technical Report No. 15, Ministry for the Environment, Wellington.

Taylor Jr GE, Norby RJ, McLaughlin SB, Johnson AH, Turner RS 1986. Carbon dioxide assimilation and growth of red spruce (*Picea rubens* Sarg.) seedlings in response to ozone, precipitation chemistry, and soil type. Oecologia (Berlin) 70: 163-171.

Tate G 2003. Fluoride monitoring of wine grapes foliage at Brookfield's Farm vineyard. Report to Hawke's Bay Regional Council and Ravensdown Fertiliser Co-op Ltd. June 2003. Crop Health Services, Huntly.

Tate G 2005. Fluoride monitoring of wine grapes and apple foliage at Brookfield's Farm vineyards and other sites. Report to Hawke's Bay Regional Council and Ravensdown Fertiliser Co-op Ltd. June 2005. Crop Health Services, Huntly.

Tough HJ, Park DG, Crutchley KJ, Bartholomew FB, Craig G 1998. Effect of crop load on mineral status, maturity and quality of 'Braeburn' (*Malus domestica* Borkh.) apple fruit. Acta Hortic 464: 53-58.

Trail J, Murray K 2005. Discharge to air resource consent. Acid characterisation from RFC stacks. Glasson Potts Fowler, Palmerston North.

Trail J, Murray K, Mullis O, Lowe H 2005. Discharge to Air Resource Consent – Monitoring Summary. Glasson Potts Fowler, Palmerston North.

Trail J, Hill J, Murray K 2006. Discharge to Air Resource Consent – Monitoring Update Summary. Glasson Potts Fowler, Palmerston North.

Trolove S, Searle B, Sorensen I, Arnold N 2011. Monitoring of leaf fluoride concentrations in the Meenee area for 2010–11. Hastings, Plant and Food Research. SPTS no. 6081.

Trolove S, Searle B, Sorensen I, Arnold N 2012. Monitoring of leaf fluoride concentrations in the Meenee area for 2011–12. Hastings, Plant and Food Research. SPTS no. 7054.

Trolove S, Sorensen I, Arnold N, Searle B 2013. Monitoring of leaf fluoride concentrations in the Meenee area for 2012–13. Hastings, Plant and Food Research. SPTS no. 8659.

Trolove S, Sorensen I, Waldon C, Searle B 2014. Monitoring of leaf fluoride concentrations in the Meenee area for 2013–14. Hastings, Plant and Food Research. SPTS no. 10218.

Trolove S, Sorensen I, Finlayson C, Searle B 2015. Monitoring of leaf fluoride concentrations in the Meenee area for 2014–15. Hastings, Plant and Food Research. SPTS no. 11652.

Trolove S, Sorensen I, Arnold N, Searle B 2016. Monitoring of leaf fluoride concentrations in the Meenee area for 2015–16. Hastings, Plant and Food Research. SPTS no. 13330.

Trolove S, Sorensen I, Liu J, Searle B 2017. Monitoring of leaf fluoride concentrations in the Meenee area for 2016–17. Hastings, Plant and Food Research. SPTS no. 14985.

Trolove S, Sorensen I 2018. Plumpton Park site visit, March 2018. Plant and Food Research. SPTS no. 16180.

Trolove S, Sorensen I, Arnold N, Liu J, Searle B 2018. Monitoring of leaf fluoride concentrations in the Meenee area for 2017–18. Hastings, Plant and Food Research. SPTS no. 16577.

Trolove S, Sorensen I, Searle B 2019. Monitoring of leaf fluoride concentrations in the Meenee area for 2018–19. Hastings, Plant and Food Research. SPTS no. 18100.

Trolove S 2020. Effects of air emissions from the Napier Superphosphate Works on vegetation, and influences of proposed stack modifications. Plant and Food Research. SPTS no. 20123.

Trolove S, Sorensen I, Searle B 2020. Monitoring of leaf fluoride concentrations in the Meenee area for 2019–20. Hastings, Plant and Food Research. SPTS no. 19591.

Trolove S, Sorensen I. 2021. Monitoring leaf fluoride concentrations in the Meeanee area for 2020–21. Hastings, Plant and Food Research. SPTS no. 21248.

Van Ryn DM, Lassoie JP, Jacobsen JS. 1988. Effects of acid mist on *in vivo* pollen tube growth in red maple. Can J For Res 18: 1049-1052.

Weinstein LH, Davison AW 2004. Fluorides in the environment. Effects on plants and animals. CABI Publishing, Wallingford, UK.

Weir RG, Cresswell GC 1993. Plant Nutrient Disorders 1: Temperate and Subtropical Fruit and Nut Crops. Melbourne, Inkata Press. 93 p.

WSU 2020. Physiological disorders tree fruit postharvest export education. Washington State University Extension http://tfrec.cahnrs.wsu.edu/postharvest-export/physiological-disorders/ [accessed 17 July 2020].

Appendix 1. Investigations of complaints made since 2008

1a. Dewar's orchard

Symptoms

On 20 April 2016, Dr Bruce Searle and Dr Stephen Trolove from Plant & Food Research, and Andrew Gass from HBRC were called out to Brett Dewar's property to investigate some round brown pitting on his 'Fuji' apples (Figure 14–16). The pitting was predominantly on the side of the apple facing the sun, and in a bunch of apples, was worst in the apple receiving the most sun. Affected apples seemed to be randomly distributed throughout the 6.5 rows that we picked. The affected apples were all over the trees (i.e. some high, some low) but generally followed the same distribution as the bulk of the apples on the trees. Occasionally one tree would have more affected apples than other trees. Brett said that he noticed more apples on the bottom tier, and generally more defects down the south eastern end of the orchard. The fruit was slow to colour-up, so was left longer to hang on the trees than a normal season.

Figure 14. Round brown blotches on Brett Dewar's apples (right). Note that the lenticel appears as a dark black spot in the centre of the brown circular blotch (below).

Figure 15. The symptoms were very shallow, limited to the peel.

Figure 16. Symptoms were predominantly on the sunlit side of the apple, and tended to be towards the calyx end of the apple.

Soil moisture

The fact that the symptoms were worse on the side of the apples facing the sun gave rise to the idea that the symptoms may in some way be caused by high temperatures, or moisture stress. Brett was saying he assumes 28 mm of evapotranspiration a week, and irrigates to 75% of this. Two holes were dug by trees that were showing more apples with symptoms than most other trees. The soil appeared to be on the dry side. Samples showed a gravimetric water content of 18 and 23 g/g, which is quite dry for harvest time. Brett was saying that this is the driest block on his orchard.

Tissue analysis

On 9 May 2016, Stephen Trolove and Bruce Searle went back out to Brett Dewar's farm to pick apples to send for analysis. Samples were collected from the 'Fuji' block, from the seven rows nearest the alder hedge. Fifteen apples were picked for each sample, with paired samples being collected from the same or nearby branches on the same tree. Three paired samples were collected. Sampling was blocked, Block 1 were from the two rows nearest the alders, Block 2 from the three rows in the middle, and Block 3 from the remaining two rows (we did not need to go down the western side of the seventh row, because we had managed to collect enough apples. Forty-five affected apples were found in 6.5 rows, therefore the number of affected apples was not high, perhaps 2% or less in these 6.5 rows. The apples may have already had a first pick on these rows, so it was not possible to quantify as a % of the total crop).

Samples were placed in the coolstore, then sent to Hill Laboratories for analysis on 11 May 2016. Apples were quartered. Two quarters from each apple were peeled and the unwashed skins were dried at 62°C, ground, and then extracted in 0.1 M perchloric acid, then measured for F by F-sensitive electrode. This is the same laboratory method that is used for leaf analysis, but the recovery method has not been used on skins before. The remaining quarters were pulped and analysed for the complete nutrient profile, and results expressed on a fresh weight basis (Table 8).

The analytical results did not detect any F, indicating that the F concentration in the skins was <1 mg/kg. A one-tailed t-test suggested Ca was lower in apples with symptoms than in apples that did not have symptoms (Table 8). Similarly, a one-tailed t-test showed that the ratio of (K+Mg)/Ca was higher in apples with symptoms than in apples without symptoms. There were no other significant differences in nutrient composition between apples with and without symptoms (Table 8).

Table 8. Whole apple nutrient concentrations (mg/100 g) as analysed by Hill Laboratories, and fruit weight (g/apple). The data are a mean of three samples. *p*-values for a two-tailed t-test are provided, except a one-tailed t test was used to test the hypotheses that the Ca concentration and fruit weight was lower in the fruit with symptoms, and that the (K+Mg)/Ca and N/Ca ratios were higher in the fruit with symptoms.

Symptoms	Ca	K	Mg	N	P	S	Na	Fe	Mn	Zn	Cu	B	(K+Mg)/Ca	N/P	N/Ca	weight
With	2.6	138	5.1	54	12	4.0	2.6	0.083	0.030	0.010	0.060	0.43	55	4.7	21	227
Without	3.5	133	4.9	42	11	3.8	2.7	0.087	0.030	0.010	0.057	0.43	40	3.8	12	239
p	0.052	0.07	0.27	0.34	0.22	0.35	0.27	0.42	*	0.42	0.42	0.81	0.040	0.46	0.11	0.25

*Data were identical for all replicates of both samples

Weather records

Table 9. Times and durations of possible exposures to emissions from the Napier Works for the 7 weeks prior to the 20/4/2016 investigation on Dewar's orchard. Short-term exposures (<20 min in 24 h) are not included. Exposure risk from the Manufacturing Plant (man. plant) is presented in minutes, and risk of acid exposure from the Acid Plant is indicated by whether there was a cold start-up during this period. Note that intermittent exposure occurred in all cases, since the time of day is longer than the wind exposure time.

Date	Time of day	Wind from Napier Works over Dewar's (min)	Humidity (%)	Wind run (km)	Superphosphate manufacturing?	Exposure to man. plant emissions (min)	Cold start-ups?	Comments
1 March	10:00–22:00	70	72–84	17	From 18:00 onwards*	20	No	*There was 20 min of wind blowing from Napier Works over Dewar's after 18:00
4 March	9:10–20:00	50	67–74	7	No	0	No	
15 March	9:50–18:40	70	70–85	14	No	0	No	
17 March	12:50–15:40	40	91–92	11	No	0	No	
9 April	15:50–22:10	100	89–91	25	No	0	Yes*	*Only on pilot light so virtually no emissions

Weather records from the Napier Works for March and April prior to 20 April 2016 were reviewed for wind events that blew from the Manufacturing Stack over the Dewar block (between 108° and 113.5°). Records showed that wind blew over the Dewar's block for a total of 9 hours over this time period, for a total wind run of 108 km. Periods where the wind blew for a substantial period of time (>20 min in 24 h) are given in Table 9. However, of these possible exposure periods, the Manufacturing Plant was only operating on one of these days – 1 March 2020. On this day, the works began operating at 18:00, and from this time onwards the wind only blew over Dewar's orchard for 20 minutes, which is insufficient time for substantial F or acid exposure. Data from the Acid Plant indicates only one cold start during these possible exposure times, and the plant was only at the pre-heating phase, so any acidic emissions would have been low. These records indicate it was highly unlikely that emissions from the Napier Works caused the symptoms observed on 20 April 2016.

Expert opinion

To the untrained eye it might be mistaken for the disease Elsinoe, but Peter Wood (Pathologist, Plant & Food Research) viewed it under a microscope and confirmed that it was not Elsinoe. Peter thought it was Ca deficiency exacerbated by water stress on the sunlit side (bitter pit). Jason Johnston (Post Harvest Physiologist, Plant & Food Research) thought it was lenticel breakdown, caused by something damaging the lenticels. He said that he had seen the same symptoms on apple fruit from another orchard this season, located on Thompson Road, Havelock North, which is over 10 km from the Napier Works Manufacturing Stacks. He showed me pictures from the block on Thompson Road, with the black lenticel and the brown circle around the lenticel. He said that the Thompson Road block was also struggling with water [i.e. quite dry].

Murray Oliver (Plant Physiology Group, Plant & Food Research) thought it was lenticel blotch caused by low Ca.

Bruce Searle and Isabelle Sorensen (Crop Physiology, Plant & Food Research) were confident it was not acid damage because the symptoms looked different to those they had seen in experiments where they had sprayed stack liquor on fruit. Also, if it was acid damage, there should have been symptoms on the leaves, but there was none on the apple trees. Although Isabelle did find some alder leaves with brown edges 2 weeks later on about four of the trees.

My (Stephen Trolove's) conclusion was that this problem was lenticel breakdown, or possibly lenticel blotch pit. This was based on the fact that every brown spot was based around a black lenticel. It was certainly not burn from acid, in which case the injury would be random with respect to lenticel location, and be located on the side of the fruit that may have received the “acidic spray droplets” or concentrated around the drip point of the fruit. There would also be damage to the surrounding leaves. ‘Fuji’ are known to be susceptible to lenticel breakdown (OMAFRA 2009). The symptoms were shallow in the apple, as is the case with lenticel breakdown, not deep like bitter pit or lenticel blotch pit (WSU 2020). The symptoms were also almost always circular, as described for lenticel breakdown, whereas lenticel blotch pit is more irregular than circular. The only fact that does not agree with the described symptoms for lenticel breakdown is that the symptoms were observed on the sunlit side of the apple (as is the case with lenticel blotch pit), whereas lenticel breakdown is usually on the shaded side of the apple (WSU 2020). Also, like lenticel blotch pit, the symptoms were generally down the calyx end of the apple. Symptoms of lenticel breakdown usually appear after packing (OMAFRA 2009); however, in this season the symptoms appeared while the fruit was still on the tree, but the fruit was left to hang on the tree much later than usual to allow it to colour up.

Fruit at greater risk of developing lenticel breakdown have high (K+Mg):Ca and N:Ca ratios (Blakey 2018), as observed in the samples taken on Dewar's orchard. New Zealand research indicates that the risk of lenticel disorders increases on trees with light crop loads (Tough et al. 1998). There is a hypothesis that lenticel breakdown is aggravated by tank dump chemicals, surfactants, detergent and waxes (OMAFRA 2009). Although this article does not specifically mention acids or F, someone may argue that chemicals from the Ravensdown stack may have in some way aggravated the problem. The fact that there was only 20 minutes of exposure to wind from the Napier Works and that F concentrations were undetectable suggests that the possibility that emissions from the Napier Works contributed to the problem is highly unlikely. In addition, this lenticel disorder was also observed in the same season in fruit at Thompson Road, which is over 10 km from the Napier Works and would not have been influenced by emissions from the Napier Works (Figure 9), indicating that the presence of stack emissions was not a necessary factor for the development of this disorder. Calcium uptake is reduced by water stress (Haber et al. 1983), which fits the occurrence of this lenticel disorder at the Thompson and Dewar orchard. Leaf F concentrations from the nearby alders that are monitored every month at the Dewar property were at similar, or lower, concentrations to other seasons (Trolove et al. 2016), suggesting that no unusually high emissions had occurred over the season. The laboratory results showed that all skins had F concentrations of <1 mg/kg. To cause damage, even in sensitive plant species, tissue F concentrations would need to exceed 20 mg/kg (Mitchell et al. 1981). The fact that we could not measure any eliminates the possibility that F had caused the symptoms observed.

Conclusion

The distribution of the injury symptoms around the lenticel in every case, and the lack of any damage on leaves, rule out acid damage. The undetectable levels of F in the apple skins, and low leaf concentrations throughout the growing season on the nearby alder shelterbelt, rule out F damage. This is supported by the weather and manufacturing data, which indicate very limited exposure to emissions prior to symptom development. The visible symptoms and fruit analysis suggest that the disorder is lenticel breakdown, which was also seen to occur in Hawke's Bay >10 km from the Napier Works during the 2015/16 season, where damage would not be caused or exacerbated by stack emissions.

1b. Plumpton Park

Introduction

An investigation was conducted at the request of Ravensdown Limited following a complaint by Mike McCabe from Plumpton Park, that trees on his property showed symptoms that looked like burn damage, which he believed was due to emissions from Ravensdown's Awatoto superphosphate plant. The symptoms were first observed in January 2018, although he was unsure of the exact date. Ravensdown approached Plant & Food Research on 5 March 2018 to visit the site, take some samples and write a report (Trolove & Sorensen 2018). A revised version, which includes weather data and the Napier Works operating times, and minor edits, is included below.

Materials and methods

A site visit was conducted on 9 March 2018. Mike McCabe, the owner of Plumpton Park, met us and explained the signs of damage he observed. Photos were taken of the symptoms pointed out by Mr McCabe. Paired samples of 30 leaves each were taken, using new nitrile gloves, of symptomatic and asymptomatic leaves. The first pair of samples was taken from the eastern side of the eastern-most row of a block of KORU®[4] apple trees located west of the house. The symptomatic leaves were taken to the north of the house, which was more exposed to the easterly wind, and the asymptomatic leaves were taken directly to the west of the house, where they were protected from the easterly wind by a shelter belt (Figure 17). Note that the Napier Works is located east of the house (Figure 18). The second pair of samples was taken from two black walnut trees grown on the eastern side of the house. The symptomatic leaves were collected from branches that grew above the shelterbelt and were exposed to the easterly wind, and the asymptomatic samples were collected from the base of the trees from branches that were protected from the easterly wind.

The samples were labelled and stored in a chiller over the weekend then sent to Hill Laboratories. The leaves were not washed, in case deposits on the outside also provided some clues about the observed marginal burning or rolling symptoms. The leaves were analysed for nutritional elements – nitrogen (N), phosphorus (P), potassium (K), sodium (Na), sulphur (S), calcium (Ca), magnesium (Mg), iron (Fe), manganese (Mn), zinc (Zn), copper (Cu) and boron (B) – to check if the symptoms were the result of excess or deficient concentrations. Fluoride was also included because F is one of the non-nutrient emissions from the Napier Works, and chloride was included because high concentrations may suggest salt spray damage.

[4] *Malus domestica* 'Plumac' (marketed as KORU®)

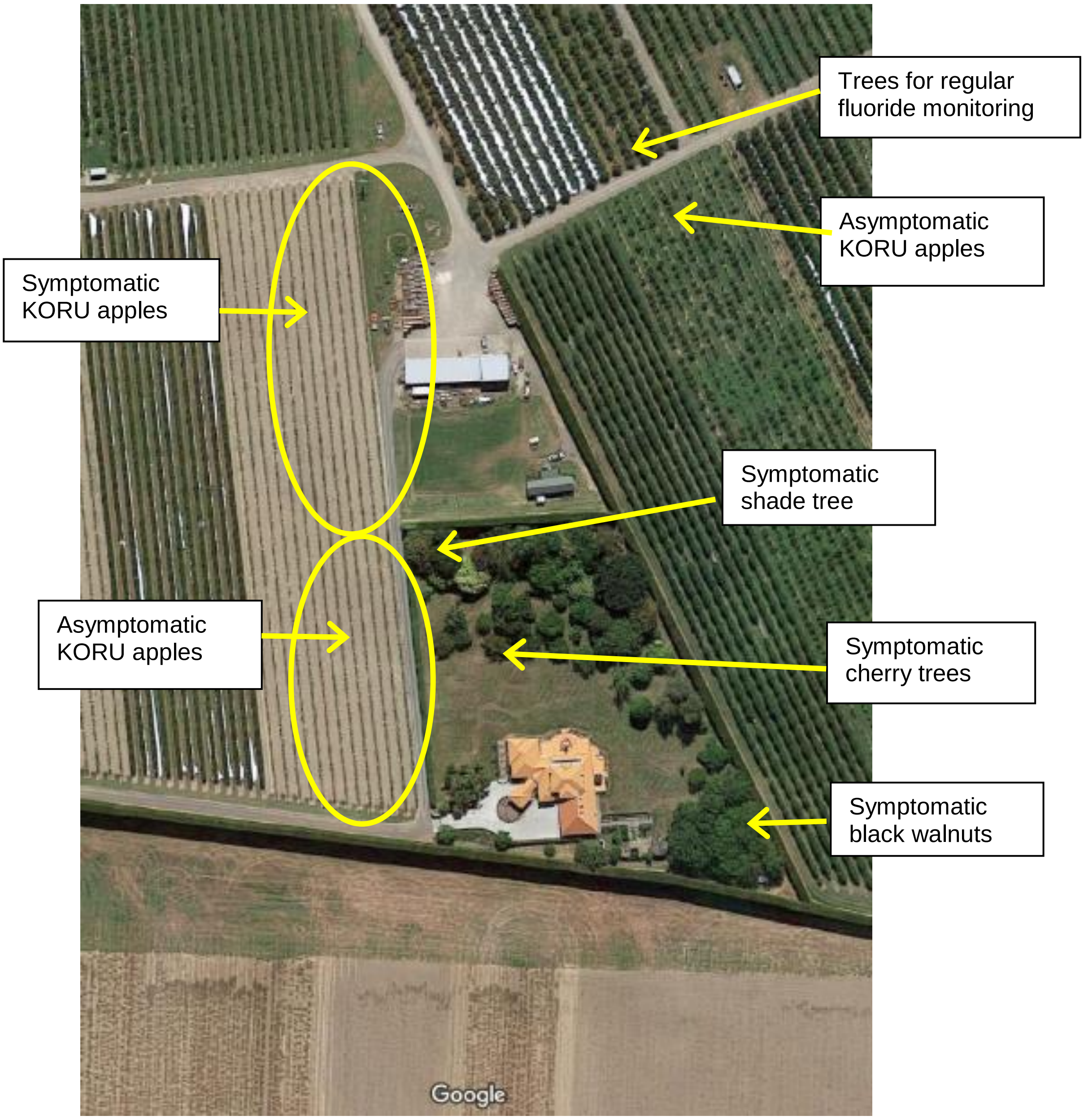

Figure 17. Google Earth satellite image of Plumpton Park showing symptomatic and asymptomatic areas. Image © 2020 TerraMetrics © 2020 Google.

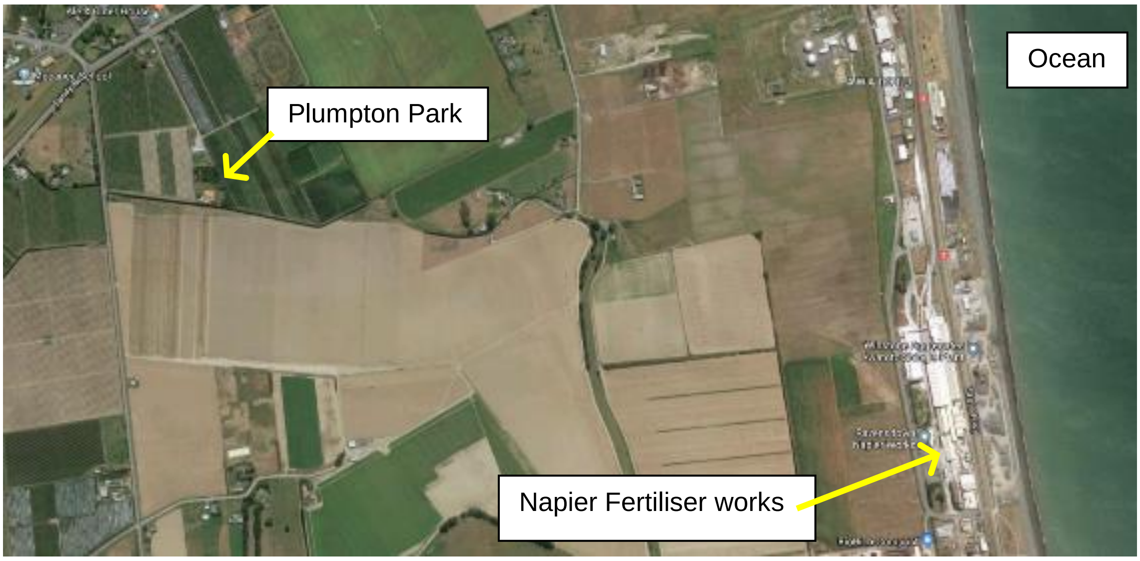

Figure 18. Google Earth satellite image showing Plumpton Park in relation to the ocean and the Awatoto fertiliser works. Plumpton Park is located 2.2 km from the Napier Works and 2.2 km from the ocean. Image © 2020 TerraMetrics © 2020 Google.

Observations and laboratory results

Mr McCabe reported that the suite of symptoms observed since January were similar to those several years ago when he took Ravensdown to court over alleged discharge damage from their Napier Works.

Apple leaves

KORU apple leaves were rolled in trees that were exposed to the easterly wind out from the shelter of the shelterbelt (Figure 19 and Figure 20), whereas KORU leaves behind the shelterbelt did not show signs of rolling (Figure 21). There was a very occasional boat-shaped leaf, amongst the rolled leaves (Figure 20). Mr McCabe said he noticed no decline in yield on the trees that showed symptoms, although possibly they may have been a bit smaller. There was no opportunity to measure this since the trees had already been picked twice. There were some leaves with burnt margins, but these were acknowledged to be unrelated to the rolling symptoms. There was a nearby block of KORU that was asymptomatic (Figure 17).

Figure 19. Apple leaves away from the shelter belt were more obviously rolled and showed bronzing on the outer edges of the underside of the leaf, compared with leaves behind the shelter belt (Figure 21).

Figure 20. Occasional boat-shaped leaves evident in leaves away from the shelter belt.

Figure 21. Leaves from apple trees growing behind the shelter belt showed much less rolling and no bronzing on the undersides of the leaves.

Black walnuts

The black walnuts were situated on the eastern corner of the lawn behind a shelterbelt. Leaves located above the shelterbelt had black, burnt margins, with chlorosis evident near the blackened margins and between the veins (Figure 22). The leaf edges were also severely damaged (Figure 22). Leaves below the shelterbelt had no chlorosis nor blackened margins, and were considerably larger than those above the shelterbelt (Figure 23).

Figure 22. Black walnut leaves showing burnt margins and burnt interveinal patches. The leaf edges were also severely damaged.

Figure 23. Symptomatic (right) and asymptomatic (left) black walnut leaves. Symptomatic leaves were much smaller, chlorotic and had burnt black margins. Leaves were collected from the same trees, with symptomatic leaves collected above shelterbelt height, and asymptomatic leaves collected below shelterbelt height, on the leeward side.

Leaf analyses

Apples

The main difference in chemical composition between the apple leaf samples was that those with symptoms had higher concentrations of Na and Cl (Table 10).

Black walnuts

There were large differences (>20%) in the concentrations of all nutrients between leaves that showed symptoms and leaves that did not show symptoms, except for Fe, Zn and Cl (Table 10). This suggests that it is not a deficiency or toxicity of one or two nutrients, but rather a more general physiological stress that is affecting nutrient uptake and distribution.

Table 10. Chemical analysis of apple and walnut leaves showing symptoms of ill health and unaffected leaves. *Normal nutrient concentrations of leaves sampled in mid-summer (Weir & Cresswell 1993).

	N	P	K	S	Ca	Mg	Na	Fe	Mn	Zn	Cu	B	Cl	F
	%							mg/kg						
Apple														
No symptoms	2.3	0.24	1.5	0.15	2.55	0.22	0.009	62	36	61	6	39	0.17	< 1
Symptoms	2.2	0.15	1.1	0.15	2.17	0.25	0.059	91	29	44	6	36	0.48	< 1
*Normal	2–2.4	0.15–0.2	1.11.5	0.2–0.4	1.1–2.0	0.21–0.4	<0.02		25–100	16–50	6–20	21–60	<0.4	
Walnut														
No symptoms	3.5	0.22	1.4	0.19	3.57	0.43	0.018	90	47	35	12	136	1.06	5
Symptoms	2.2	0.42	3.7	0.41	1.1	0.24	0.124	84	65	41	9	15	1.25	7
*Normal	2.2–2.9	0.1–0.29	1.0	2.0	1.2–2.5	0.2–0.5	0–0.1		25–300	20–200	4–50	25–100	0–0.3	

Cherry leaves

Two cherry trees had rolled leaves on the upper branches, whereas the shaded lower branches were normal (unrolled, Figure 24 and Figure 25). Mr McCabe stated that this would not be due to water stress, since the water table was only approximately “the depth of a fence-post" (c. 1.2 m) below the soil surface, and he had only needed to irrigate about five times that season. Mr McCabe confirmed that he used a commercial water monitoring service.

Figure 24. Cherry tree with rolled leaves on the outermost branches, and normal unrolled leaves in the shaded lower branches.

Figure 25. Close-up of cherry tree leaves.

Shade trees

A large shade tree on the north-western end of the property had brown leaves on the top eastern side of the tree above the shelterbelt, whereas the leaves on the western side or below the shelter belt were green (Figure 26).

A silver birch located on the east side of the property also showed similar symptoms above the shelter belt, but had healthy leaves below the shelter belt. There were also noticeably fewer leaves on branches above the shelter belt.

Figure 26. A large tree protruding above the shelter belt with browning on the leaves on the north-eastern side. There is no browning on the shelter belt.

Weather and manufacturing records

Weather records from the Napier Works from 15 December 2017 to 31 January 2018 were reviewed for wind events that blew from the Manufacturing Stack over Plumpton Park (between 106.1° and 116.1°). Records showed that wind blew over Plumpton Park orchard for a total of 24.3 hours over this time period, for a total wind run of 269 km. Periods where the wind blew for a substantial period of time (>20 min in 24 h) are given in Table 11. These records confirmed that the wind was blowing from the Napier Works across Plumpton Park prior to the complaint, although this does not necessarily mean that the injury was caused by the Napier Works. Two periods of exposure were for over 2 hours over a period of 3 days, and three periods were for half an hour (Table 11).

Table 11. Times and durations of possible exposures (>20 min in 24 h) for Plumpton Park orchard (106.1–116.1°) to emissions from the Manufacturing Plant (man. plant) at the Napier Works from 15 December 2017 to 31 January 2018. Short-term exposures (<20 min in 24 h) are not included. Exposure risk from the man. plant is presented in minutes, and risk of acid exposure from the Acid Plant is indicated by whether there was a cold start-up during this period. Note that intermittent exposure occurred in cases where the interval between start and end time is greater than the total exposure time.

Start time	End time	Wind from Napier Works over Plumpton Park (min)	Humidity (%)	Wind run (km)	Man. plant operating?	Man. plant comments	Exposure to man. plant emissions (min)	Cold start-ups?	Acid Plant comments
8:40 Dec 22	14:30 Dec 22	140	66–78	30	No		0	No	Plant off
14:00 Dec 26	18:10 Dec 26	90	76–81	20	No		0	No	Plant off
22:10 Dec 31	22:50 Dec 31	40	71–73	4	No		0	No	Plant off
20:50 1 Jan	6:50 Jan 3	210	82–86	35	No		0	No	Plant off
19:20 Jan 9	20:20 Jan 13	30	77–85	106	Yes		30	No	Plant off
1:50 Jan 15	6:20 Jan 15	30	84–89	4	Yes		30	Yes	Plant in start mode, heating through with diesel. Sulphur on 14:55 Jan 16
19:10 Jan 19	22:30 Jan 21	150	54–77	32	Yes	Plant off 06:24–09:28 Jan 21	150	No	Plant on
12:40 Jan 26	14:20 Jan 26	30	66–67	7	Yes		30	No	Plant on
20:50 Jan 27	9:20 Jan 29	130	73–84	20	Yes	Plant off 06:33–11:05 Jan 27	130	No	Plant on

Discussion

Apple leaves

The symptomatic KORU apple leaves showed signs of rolling and bronzing on the underside of the leaves. Leaf rolling can be caused by a number of factors, including water stress (Nemeskeri et al. 2015). Leaf rolling exposes the more sensitive undersides of the leaves to sunburn (Weir & Cresswell 1993). Mildew also causes bronzing. There were some boat-shaped leaves (Figure 20). Boat-shaped leaves can be caused by concentrated sulphuric acid. Application of sulphuric acid at pH 1.4 has been shown to increase the risk of boat-shaped leaves when applied to 'Sciearly'/Pacific Beauty™ apples during 50% flowering, but the risk of boat-shaped leaves was very low when acid was applied when the fruit was large (Searle et al. 2007a), as was the case at Plumpton Park. Furthermore, no boat-shaped leaves were observed when sprayed with sulphuric acid or stack liquor at a pH of 2.7 (Searle et al. 2007a), and since 2008 the pH of emissions from the Manufacturing Stack has been adjusted to >2.7. Also, the risk of acid damage from the Acid Plant is low over the period of interest (mid-December to the end of January), since there were no cold starts when the wind was blowing in the direction of Plumpton Park (Table 11). Thus it is unlikely that the boat-shaped leaves are due to acidity.

The higher concentration of Na and Cl in the symptomatic apple leaves concurs with the location of the apple trees showing symptoms being exposed to salt spray from the easterly wind, whereas apple trees that showed no symptoms were protected from the easterly wind by the shelterbelt. There was no difference in leaf S or F content, suggesting no difference in exposure to S or F that may have come from the Awatoto superphosphate plant. Other tree physiology staff at Plant & Food Research also thought that the observed symptoms were the result of wind damage, without having been told anything about the history or location of the leaves.

Black walnuts

The burnt margins on the walnut trees were claimed by Mr McCabe to be the result of acid burn from the Ravensdown Plant. Studies of acid burn patterns from spray trials conducted by Searle et al. (2007a) show that spraying apple leaves with concentrated sulphuric acid caused burnt spots where the droplets landed, and also burnt margins where the acid spread towards the margins (Figure 27). The edges of the burn marks were distinct, with no evidence of chlorosis (yellowing) at the edges of the burn. Leaves collected from the black walnuts on Mr McCabe's property also showed marginal burn, with some burnt patches in the centre of the leaves (Figure 22). Some burn marks had distinct edges, and others had gradual edges with burn marks intergrading into chlorosis (Figure 22). The burnt patches tended to be interveinal, and were less obviously 'droplet shaped' than those in Figure 27.

Figure 27. Burn symptoms on apple leaves caused by spraying sulphuric acid at pH 1.4 (Searle et al. 2007a).

If the observed damage was due to acid burn, and the leaves were sampled immediately after the symptoms were observed, then we might expect to see very similar leaf concentrations between the affected and unaffected leaves, with elevated F and/or S concentrations only in the affected leaves. So while the S concentration of symptomatic walnut leaves was more than twice that of the asymptomatic leaves (Table 10), the concentrations of almost all the nutrients were different, suggesting that whatever stress the leaves are experiencing is affecting nutrient uptake of the plant. For example, K was more than double in the symptomatic leaves; it is unlikely that this came from the Ravensdown stack because stack K emissions are very low, but very likely that this K came from the soil, so it appears that the stress is affecting plant uptake. So the source of the extra S in the symptomatic leaves may be from the soil, not necessarily from the Napier Works. A factor that may affect the accuracy of any diagnosis is that the leaf samples were taken more than 1 month after the symptoms were observed, so the stress in January may have resulted in subsequent differences in nutrient uptake between the affected and non-affected leaves, making diagnosis of the original problem difficult, and certainly beyond the scope of this report.

Combining the leaf analysis information from both the walnuts and the apples can also help shed light on whether the symptoms were that result of acid burn. If we assume that the damage to the walnuts was the result of sulphuric acid burn, the question remains as to why the apple leaves on exposed trees did not have higher S concentration than leaves on trees protected from the wind.

Strong wind and salt spray can also cause burnt and severely damaged leaf edges (Figure 28). The tree in Figure 28 was located 5.1 km from the Ravensdown stack, and the north side of the tree, where the damage symptoms were evident, would have been sheltered from emissions from the Ravensdown stack. However, the north side was exposed to salt winds, being located only 200 m from the ocean.

Figure 28. A leaf from the south (left) and north (right) side of a maple tree growing at 53 McGrath St, Napier. The south side was protected from the wind by other trees, whereas the leaves on the north and east sides were exposed to the salt wind. Photo taken 16 March 2018.

Wind damage would also explain the tattered appearance of the leaves (Figure 22), and the fact that the symptoms appeared only on the walnut leaves above the shelter belt, or on the apple leaves out to the side of the shelter belt. The leaf analysis was not definitive in identifying salt damage as the cause. The leaves with symptoms had only a 17% higher Cl concentration than the healthy leaves. The leaf Na concentration is nearly six times higher in the symptomatic leaves, which suggests exposure to salt spray. According to Weir and Cresswell (1993), toxic concentrations of Cl in walnuts may occur at leaf concentrations anywhere between 0.6 and 3.3%.

Fluoride damage was also a possibility if the Napier Works is suggested as a cause. Hydrofluoric acid caused the marginal burn symptoms in Figure 29. The leaf F concentration was 40% higher in the symptomatic leaves on the Plumpton Park property, indicating more exposure to F. However, the leaf F concentrations in the symptomatic leaves were low (Table 10), well below 10 mg F/kg. Concentrations of F below 10 mg/kg are considered to be within the normal range (Doley 2006b) and there have been no reports of damage to plants below 10 mg/kg.

Other unusual results from the leaf analysis was that the symptomatic leaves were low in B, and high in P and K. These tissue concentrations of B, P or K are unlikely to have caused the observed symptoms. The asymptomatic leaves were high in Ca.

Figure 29. Grape leaves affected by atmospheric hydrofluoric acid (Source: Weir and Cresswell 1993).

Cherry trees

The rolled leaves on the uppermost branches of cherry trees at Plumpton Park has also been observed in a cherry tree in Avondale Road, Taradale (Figure 30). This tree is located 6.5 km from the Napier Works, which is well outside the 2.5 km distance that is the normal limit for the influence of F from the Napier Works (Figure 9). The rolled leaves symptoms in the Taradale tree also appeared in January, which was particularly dry. The same symptoms were also observed in a cherry tree on St George’s Road near Havelock North and in Coverdale Street, Napier, on 16 March 2018. Rolled leaves can be caused by water stress. Rolled leaves can also be caused by a heavy infestation of sucking insects or disease, but these were not observed at Plumpton Park. Rolled leaves can also be a sign that the tree is healthy and producing excess carbohydrate. Rolled leaves have been noted on apple trees carrying a very light fruit load, but not on a heavy cropping tree (Ben van Hooijdonk, pers. comm.). This would be a more likely explanation given that the water table was said to be approximately 1.2 m below the soil surface.

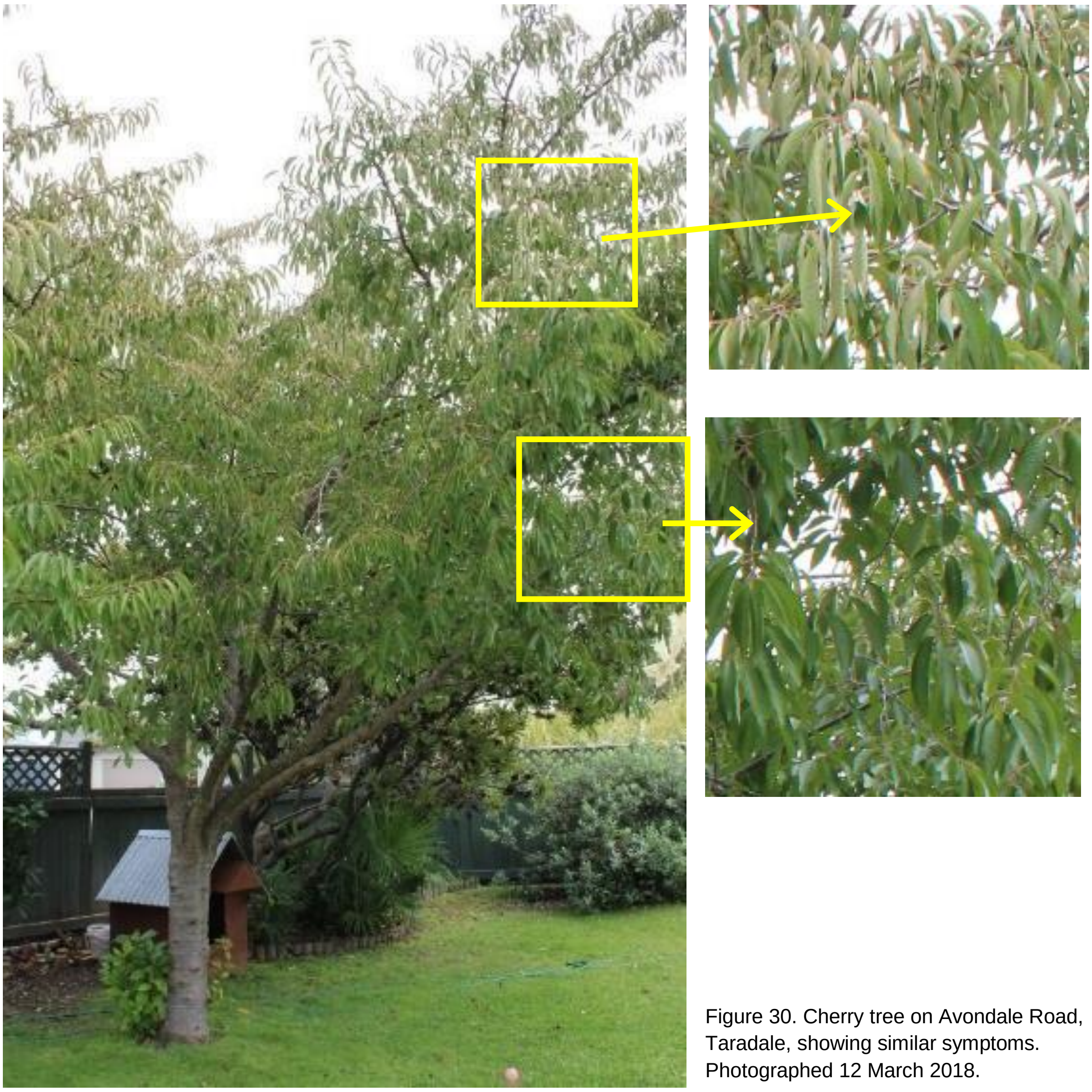

Figure 30. Cherry tree on Avondale Road, Taradale, showing similar symptoms. Photographed 12 March 2018.

Summary and conclusions

The three possible causes of damage from the Napier Works are: F damage, acid damage from the Manufacturing Stack, or acid damage from the Acid Plant, or a combination of all three. Leaf F concentrations were undetectable in the apple leaves, and low in the walnut leaves, indicating that the damage was not due to F. Acid damage from the Manufacturing Plant is unlikely, since the pH of all emissions is now adjusted to >2.7, and also the acidity would have been accompanied by F, but this was undetectable in the symptomatic apple leaves. The third possibility is that the damage is the result of emissions from the Acid Plant. In the previous resource consent period this was believed to have been associated with cold starts. The weather and manufacturing data shows that there were no cold starts when the wind was blowing from the Napier Works over Plumpton Park (Table 11). The patterns of necrosis are not consistent with acid damage, and the leaf analysis results are not consistent with acid damage. We therefore conclude that the damage was not a consequence of emissions from the Napier Works.

The walnut leaves had severely damaged edges, which is consistent with wind damage. High Na in leaves of both affected apple and walnut also support the hypothesis of damage from salt-laden wind. The dry weather in January would have exacerbated the symptoms of wind damage and can contribute to the observed leaf rolling. The delay of more than a month between the symptoms appearing and leaf sampling made it difficult to identify the cause of the leaf stress. The rolled leaves on the cherry trees were also observed at a range of locations around Hawke’s Bay that are outside the normal range of F deposits from the Ravensdown stack, and so are unlikely to be the consequence of damage from the stack.

Appendix 2. Waitangi Regional Park

2a. First visit

Stephen Trolove from Plant & Food Research visited the cycle-way and Waitangi Regional Park on 27 July 2020 to assess vegetation for any visible signs of tissue damage that may have arisen from the Napier Works. The trees visited are shown in Figure 31. The route focused on plants most likely to show any signs of damage, which included plants closest to the Napier works and F-sensitive plants that were close to the works. The plants observed were amenity trees and shrubs, no attention was paid to weeds, because the general public is unlikely to be concerned about the appearance of weeds, e.g. boxthorn, pampas and herbaceous weeds.

Figure 31. Places visited at Waitangi Regional Park.

Ngaios along the cycleway

The first shrubs visited were the ngaios (*Myoporum laetum*) along the cycleway southeast of the Napier Works. These were the closest amenity plants to the Napier Works. There is no information on the F tolerance of *M. laetum*, but it is likely that this species is tolerant, since other members of this genus (*Myopurum acuminatum* and *M. insulare)* are tolerant (Doley et al. 2004), and *M. laetum* is a coastal plant and most coastal plants are tolerant of F (Doley pers. comm.). Overall, these ngaios appeared healthy (Figure 32 top) and the authors consider that the general public would not be concerned about the health or appearance of these plants. Photos taken of the north-northwestern side of the ngaio bushes facing the Napier works show the foliage appeared healthy (Figure 32). Foliage on the north-eastern and eastern side of the ngaio bushes showed occasional browning of some of the older leaves nearer the tip, and some tip burn and pinching of other leaves (Figure 33 and Figure 34). This was considered likely to be attributable to salt damage, since the eastern side of the bushes faced the ocean, and similar but more extreme symptoms were observed on a ngaio bush growing closer to the ocean (Figure 35). This bush had a lost a large number of leaves on the eastern side (which faces the ocean, Figure 35), and many leaves on the eastern side showed brown tips (Figure 36), there were much less leaves with brown tips on the other sides of the bush. Therefore, the brown tip damage on this ngaio was assumed to be the result of salt wind damage. These symptoms were similar to those observed on a ngaio also growing right next to the ocean at Haumoana (Figure 37), which is located 7.5 km from the Napier Works and therefore considered to be unaffected by emissions from the Napier Works. The foliage on the northern side of other ngaio bushes southeast of the Napier Works was inspected for signs of possible damage from the Napier Works, and they also appeared healthy.

Figure 32. Photos of the ngaio closest to the south-west side of the Napier Works. The photos are of the north-northwestern side of the shrub, which faces the Manufacturing Plant. The top is more distant; the photo below is closer. Photos taken 27/7/20.

Figure 33. Leaves on the ngaio bushes closest to the south-west side of the Napier Works. Photos taken of the north-eastern side. There was some browning on the leaf tips. Photos taken 27/7/20.

Figure 34. Damage to some leaves on the ngaios closest to the south-west side of the Napier Works. Left: An old leaf with a pale brown tip, and some mild chlorosis. Right: Leaf with a dark brown tip, with some pinching. Photos taken 27/7/20.

Figure 35. The eastern side of a ngaio bush, located 22 m from the ocean (at high tide). Photo taken 27/7/20.

Figure 36. Brown tips on the leaves on the eastern side of the ngaio in Figure 35, assumed to be caused by salt damage. Photo taken 27/7/20.

Figure 37. Left: salt wind damage on a ngaio growing 15 m from the ocean (at high tide) at Haumoana, 7.5 km from the Napier Works. Right: the ngaio at Haumoana. Photo taken 27/7/20.

Pohutukawa trees around the Kirsa Jensen Memorial

Pohutukawa trees (*Metrosideros excelsa*) planted around the Kirsa Jensen Memorial (735 m south-southeast of the Manufacturing Stack and 30 m from the ocean at high tide) were also investigated for signs of emissions damage. Pohutukawa has intermediate tolerance of F (Doley et al. 2004). These pohutukawa trees were very open, with most of the foliage growing on the western side away from the ocean (Figure 38). The foliage generally appeared healthy (Figure 39), with some leaves showing some chlorosis or brown tips (Figure 40). There did not appear to be a pattern to the occurrence of these occasional symptoms, with both older and younger leaves affected, and the trees were so open there was not really a side that was sheltered from either ocean winds or winds from the direction of the Napier Works. The cause of these symptoms was not able to be distinguished based on the location of damage of the foliage. These occasional symptoms were also evident on pohutukawa trees located 8 km from the Napier Works at Haumoana (Figure 41), so were considered to be most likely salt damage. Certainly they were not present in any greater extent in trees closer to the Napier Works, and the number of leaves showing symptoms were small and did not affect the overall appearance of the tree, so the authors considered that these symptoms were not a cause for concern.

Figure 38. Pohutukawa trees growing around the Kirsa Jensen Memorial. Photo taken 27/7/20.

Figure 39. Foliage of one of the pohutukawa trees around the Kirsa Jensen memorial site. Photo taken 27/7/20.

Figure 40. A close-up of the foliage of a pohutukawa growing by the Kirsa Jensen memorial. Note the brown tips and some chlorosis at the tips of the leaves. Photo taken 27/7/20.

Figure 41. A close-up of foliage of a pohutukawa growing near Haumoana, 8.0 km from the Manufacturing Stack. Note that some of these leaves also show brown tips or chlorosis at the tips or margins. Photo taken 3/8/2020.

Native trees around Horseshoe Wetland at Waitangi Regional Park

A range of native trees are growing near the lake at the Waitangi Regional Park. Two isolated cabbage trees were growing closer to the Napier Works than the others (Figure 42), and these were examined, especially since cabbage trees are known to be sensitive to F (Doley et al. 2004). If suffering from F damage, cabbage tree leaves will show a strong brown coloured die-back from the tips of otherwise healthy leaves, with distinct margins and sometimes pinching at the leaf tips (Figure 43). The leaves of the larger cabbage tree at the Waitangi Regional Park appeared healthy (Figure 44). A close examination of the leaf tips of the larger of the two cabbage trees showed a small amount of normal attrition, which was pale brown in colour (Figure 45), as opposed to the strong brown colour associated with F damage (Figure 43). Leaves from the smaller cabbage tree beside it had dark brown necrotic bands between the green part of the leaf and the pale straw-brown necrotic tips (Figure 46). These symptoms were also seen on cabbage trees near the ocean at Te Awanga, 10.4 km from the Napier Works (Figure 47), so may be a sign of salt damage. The symptoms looked quite different to the bright red-brown necrosis associated with F damage (Figure 43).

The other native trees growing on the northern side of the lake (facing the Napier Works) looked healthy. These trees were: akeake, cabbage trees, ngaio, cottonwood, harakeke, koromiko and taupata. The taupata showed some general leaf yellowing (Figure 48), but this was suspected to be related to plant nutrition, and was not a symptom that would be expected from emissions damage. The native flax (harakeke), is also sensitive to F (Doley et al. 2004), and this also looked healthy (Figure 49). None of the tree leaves showed signs of cupping or buckling. The only signs of tip burn was on a few of the lower branches of an akeake tree (Figure 50). This tree was growing closer to the ocean than the six other akeake trees, and the branches with leaves showing tip burn were exposed to the salt wind, whereas higher branches showed no symptoms but were protected from the salt wind by other trees. Both the symptomatic and asymptomatic branches would have had unobstructed exposure to any emissions from the Napier Works. Therefore, these symptoms were assumed to be most likely salt damage.

Figure 42. Two cabbage trees located 950 m south of the Napier Works in the Waitangi Regional Park. Photo taken 27/7/20.

Figure 43. Cabbage tree showing symptoms of F damage (not growing in Hawke's Bay). Note the dark brown necrosis with clear margins on an otherwise healthy leaf. Source: Kelvin Lloyd, Wildland Consultants Ltd. Used with permission.

Figure 44. One of the branches of leaves from the larger cabbage tree growing 950 m from the Napier Works. Photo taken 27/7/20.

Figure 45. Closer view of the leaf tips of the cabbage tree growing 950 m from the Napier Works. Photo taken 27/7/2020.

Figure 46. Leaves of the smaller cabbage tree growing 950 m from the Napier Works. There was a region of straw-coloured necrosis, then a darker area of necrosis with a distinct margin, and then the leaves were green, with some yellowing near the necrotic tips. Photo taken 3/8/2020.

Figure 47. Leaf tip of a healthy cabbage tree growing near the ocean at Te Awanga, 10.4 km from the Napier Works. Photo taken 3/8/2020.

Figure 48. Taupata growing at Waitangi Regional Park growing on the north side of the lake facing the Napier Works. The older leaves showed some yellowing, which is assumed to be nutritional. Photo taken 27/7/20.

Figure 49. The harakeke (native flax) at Waitangi Regional Park growing on the north side of the lake facing the Napier Works appeared healthy. Photo taken 27/7/20.

Figure 50. Tip burn on akeake leaves. This symptom appeared on the lower branches only, which were exposed to the easterly salt wind. Photo taken 27/7/20.

Conclusions from Waitangi Regional Park visit

There did not appear to be any damage to vegetation closest to the Napier Works in the Waitangi Regional Park area that was likely to have been caused by exposure to emissions from the Napier Works. Note that these observations are only relevant to the time period relating to the length of time the observed leaves have been on the trees that were examined. The only way to gauge whether damage to vegetation may have occurred previously (to a degree that would be of concern to the public) is the fact that examination of the complaints register kept by Ravensdown showed that there had been no complaints about damage to plants in the Waitangi Regional Park that were alleged to arise from emissions from the Napier Works.

2b. Second visit to the Waitangi Regional Park

Introduction

Dr Stephen Trolove visited Waitangi Regional Park on 13 August 2021, and noted browning or burn-like symptoms on the tips and edges of leaves that were more prevalent on the northern side of the young trees, which faced the Napier Works (Figure 51), than on the southern side (Figure 52). The burn-like symptoms were evident on tarata, (lemonwood, *Pittosporum eugenioides*), kohuhu (*Pittosporum tenuifolium*) and karamu (*Coprosma robusta*) and on some akeake. Tarata is reported as being sensitive to F, whereas kohuhu and karamu are listed as tolerant (Doley et al. 2014). There were no symptoms on adjacent harakeke (native flax, *Phormium tenax*) bushes or tī kōuka (cabbage trees, *Cordyline australis*), which are known to be sensitive to F (Doley 2014). These symptoms may have been caused by salt-laden ocean spray or perhaps F. Since the symptoms were worse on the side that faced the Napier Works, it was considered important to investigate the damage further.

Materials and methods

On 13 September 2021, 10 tarata and 10 karamu trees were selected for leaf sampling. The trees were in an area of new planting located immediately south of the blind arm of the Tutaekuri River and east of Highway 51. Eight leaves were collected from each young tree, four showing symptoms and four not showing symptoms. An attempt was made to collect symptom and symptomless leaves of the same age, to minimise any variation in elemental composition resulting from leaf age. Leaves were sampled from all sides of the tree if possible, to minimise any aspect bias, but leaves showing symptoms were predominantly on the top and northern side of the tree, and leaves without symptoms were generally lower on the tree and on the southern side. Leaf samples were collected using gloves, the samples were refrigerated overnight then sent to Hill Laboratories. There the leaves were acid detergent washed, then analysed for F, sodium (Na) and chloride (Cl).

Figure 51. Leaf damage on northern side of a young tarata tree. Photo taken 13 August 2021.

Figure 52. Photo of the south side of the young tarata tree in Figure 49. Note that the lower leaves show no damage. Photo taken 13 August 2021.

Results and discussion

Symptoms

Figure 53. Damage to tarata leaves. Photo taken 13 August 2021.

Figure 54. Damage to karamu leaves. Photo taken 13 September 2021.

Symptoms (Figures 53 and 54) appeared on fully expanded leaves at any point along the twig. There was very little leaf cupping. Leaf cupping is often a symptom of fluoride damage. The observed symptoms were similar to those observed on the seaward side of a tarata growing on the coast at Haumoana (Figure 55), which is 5.6 km from the factory – a distance too far to be significantly affected by any F emissions from the Napier Works.

Figure 55. Tarata at Haumoana showing signs of salt-wind damage. The side with dead branches faces the sea. The inset shows a close-up of the leaf damage. Photos taken 20 September 2021.

Leaf analysis

Leaf sample data showed that the concentrations of F, Na and Cl were all approximately twice as high in the leaves showing symptoms compared with those without symptoms (Table 12). Sodium concentrations were three times greater in symptomatic tarata leaves. Ocean spray will carry F, Na and Cl, whereas emissions from the Napier Works carry F, but very little Na or Cl.

There are no published critical element concentrations for tarata or karamu, so the concentrations are compared with those of other tree species. The leaf F concentrations in the symptomatic leaves were not high enough to be the likely cause of the browning and tip burn, since even minor damage symptoms (<10% of leaf area showing necrosis) are not usually evident in sensitive species until concentrations reach approximately 20 mg/kg (Mitchell et al. 1981). Sodium concentrations in tarata leaves were at a concentration where damage was likely, since Na concentrations over 0.25% are classified as excessive for citrus, over 0.4% for grapes, or over 0.5% for pipfruit and stonefruit (Weir & Cresswell 1993). Concentrations deemed excessive for chloride range from >0.6% for citrus to 2.5% for persimmon (Weir & Cresswell 1993).

Table 12. Element concentrations in leaves from the Waitangi Regional Park with (+) and without (-) tip-burn symptoms.

	Fluoride (F) mg/kg		Sodium (Na) %		Chloride (Cl) %	
Species	+ symptoms	- symptoms	+ symptoms	- symptoms	+ symptoms	- symptoms
Tarata	11	6	0.655	0.201	1.03	0.50
Karamu	12	5	0.192	0.079	0.90	0.69

Conclusion

The leaf analysis, scarcity of cupping symptoms, no damage to F-sensitive cabbage trees or harakeke leaves, and the similarity of the symptoms to that found on a coastal tree far from the stack, all indicate that the damage was caused by salt-laden winds, not from F emissions from the Napier Works.

Appendix 3. Testing plants of significance to mana whenua for fluoride

Background

As part of the resource consent renewal project, Ravensdown formed a Technical Focus Group ('TFG'), made up of representatives from key stakeholder groups to engage with and provide advice and input in a two-way information sharing process. Mana whenua members of the TFG wanted to understand whether there was any possibility that the emission of fluoride (F) was negatively impacting mahinga kai (wild-harvested food) that may be growing in the area. Ravensdown engaged Plant & Food Research to undertake sampling and testing of the F concentration of plants growing close to the Napier Works. The data were then sent to Dr Francesca Kelly to assess these results in the context of any effects on human health (Kelly 2021).

Methodology

Three locations were selected for sampling, as shown in Figure 56.

- The Awatoto area, including the Waitangi Estuary and drains, located adjacent to the fertiliser factory, which were therefore the most likely location to show increased F concentrations.
- The Tukituki River mouth was considered a suitable control location, since it is also located close to the coast, so would also receive any F in ocean spray, yet is far enough from Awatoto not to be significantly affected by any fluoride in emissions from the fertiliser factory (Figure 9). Samples were taken from Grange Creek, a tributary of the Tukituki River, within 1.2 km of the Tukituki River mouth.
- The Clive River at Whakatu is of importance to mana whenua, since their land and marae is located there.

Three plant species were selected for sampling:

- Watercress (kowhitiwhiti, *Nasturtium officinale*) – a common mahinga kai species.
- Horse's mane weed (*Ruppia megacarpa*) – an important food source for fish and waterfowl.
- Kukuraho (Nga raho a tuna, river bulrush, *Bolboschoenus fluviatilis*) – a species that was historically harvested for food and significant to mana whenua, who note that it is possibly the reason for the name of the area (Awatoto = blood river), due to the reddish orange-brown colour of iron oxides on the roots of this plant at times.

Sampling was carried out on 20 September 2021. Potentially edible shoots of watercress were collected, and any inedible stems or roots removed. The precise locations of plants at each location (Figure 56) are described below.

Awatoto:

- Watercress was collected from both sides of the pool at the head of the Awatoto drain, where it emerges out of the south side of the stopbank. The watercress was growing in the soil, 20–50 cm from the water's edge. The watercress was short as it had been previously grazed by stock. The watercress was also muddy as the site had recently flooded.

- Exposed kukuraho tubers were collected from the edge of the western bank of the Awatoto drain, 50–60 m south of the head of the drain.

- Horse's mane weed was collected from in the river bed of the blind arm of the Tutaekuri River.

Whakatu:

- Watercress growing in soil was collected from the edge to approximately 1 m from the northern bank of the Clive River.

Haumoana:

- Watercress growing in soil was collected from the northern bank of Grange Creek.

- Exposed kukuraho tubers were collected from the edge of both sides of Grange Creek.

- Horse's mane weed was collected from the bed of Grange Creek near the cycleway on the eastern side of the creek mouth.

Figure 56. Sampling sites. Image © 2021 TerraMetrics © 2021 Google.

All plant samples were refrigerated, then sent to Hill Laboratories the following day. They were water washed, oven dried at 62°C, ground then extracted in 0.1 M perchloric acid. Fluoride was determined using an ion sensitive electrode. Dry matter content was determined by oven drying at 105°C for 24 h. Samples for watercress and kukuraho were combined across the locations, since the amount of sample material collected was low.

Results

All plants appeared healthy. The watercress was smaller at Awatoto than at the other locations, but this is likely because the watercress appeared to have been grazed over 5 weeks prior to sampling. The horse's mane weed was shorter at Awatoto than at Haumoana.

Fluoride was below detectable concentrations in all samples except for the watercress and kukuraho at Awatoto (Table 13).

Table 13. Fluoride concentration (mg/kg dry matter) in plant samples. Note that the dry matter content of the watercress and kukuraho were 7.3 and 17.6%, respectively. Also shown is the distance (km) of the plants from the stack.

	Awatoto			Whakatu	Haumoana		
	Watercress	Kukuraho	Horse's mane weed	Watercress	Watercress	Kukuraho	Horse's mane weed
F (mg/kg)	11	34	<2	<2	<2	<2	<2
Distance	0.62	0.66	1.08	5.41	6.25	5.50	5.50

Discussion

The results show measurable concentrations of F in watercress and kukuraho, which grew within 700 m of the Napier Works, and no detectable F in samples growing further away. This suggests some effect of the Napier Works on the F concentration in these plants. An increase in plant F concentrations agrees with the findings of Trolove & Sorensen (2021), where perennial crops showed elevated F leaf concentrations within 2 km of the Napier Works. There was no increase in F concentrations in horse's mane weed sampled at Awatoto, which is within 2 km of the stack. The F concentration of horse's mane weed would not be influenced by atmospheric F concentrations, since it grows underwater, but rather F concentrations in the water or sediments, which are likely to be low in the blind arm of the Tutaekuri River (Phillips et al. 2021).

There are no specific guidelines as to what F concentrations may affect the growth of watercress or kukuraho. Fluoride concentrations of up to 20 mg/kg of dry matter are within the normal range for plants (Mengel & Kirkby 2001). The F concentration in watercress at Awatoto was within this range. Calculations by Dr Kelly (Kelly 2021) show that this concentration of F is far below the level that would be of concern to human health, if this watercress was consumed. The concentration of F in kukuraho was above this range at 34 mg/kg. Plants have widely differing sensitivities to F, with very sensitive plants showing minor leaf symptoms at just above 20 mg/kg, with other plants not showing symptoms until concentrations reach 1000 mg/kg (Doley 2005). It was not possible to examine the kukuraho for leaf symptoms, since kukuraho always dies down over winter. However, the species did seem quite abundant in the area.

Conclusions

The higher concentration of F in watercress and kukuraho collected within 700 m of the Napier Works than those sampled further away, suggests some effect of the Napier Works on the F concentration in these plants. The F concentration in the watercress at Awatoto was within the normal range commonly found in plants, and did not appear to be causing any harm. It was not possible to visually assess for effects of F on kukuraho at Awatoto, since this plant always dies down over winter. None of the other plants collected contained detectable concentrations of F, suggesting they were unaffected by the F from the Napier Works.

Appendix 4. Leaf F monitoring methodology

Leaf samples are collected monthly during the growing season – from the beginning of November until the beginning of May at all sites, according to the protocol described in Table 14. An exception is that leaves are not sampled once they turn yellow, since the dry matter (DM) decreases, which artificially inflates the leaf F concentrations (which are expressed per g of leaf DM). Yellowing commonly affects stonefruit and grape leaves, which change colour earlier than apple leaves. All sampled leaves were visually assessed for F damage.

Table 14. Protocol for leaf sampling in the fluoride (F) monitoring trial.

Number	Task
1	Samples were collected monthly.
2	Bags were labelled with site number and date.
3	At each sample site:
3.1	New gloves were put on.
3.2	Any symptoms that may be F damage (e.g. Searle et al. 2008; Rhimi et al. 2016) were noted.
3.3	Leaves were sampled.
3.4	On grapes, 80 mature leaves from the middle of the canopy were picked from selected vines. The sample was split into two bags of 40 leaves each, with one sample to be washed and one to be left unwashed.
3.5	On apples, mature leaves from the middle of the shoot were picked. A total of 60 leaves were sampled from selected trees, to be analysed as unwashed samples. Eighty leaves were collected from Sites 4, 5, 13, and 18, which were split into two bags of 40 leaves each, with one sample to be washed and one to be left unwashed.
3.6	Leaves were placed in a numbered bag, and placed in a chilly bin.
3.7	Gloves were removed and placed in a rubbish bag before moving to the next site.
4	Samples were sent to Hill Laboratories Ltd for analysis the same day – couriers were contacted for sample pickup within 1 hour of returning from sampling.

Leaves are then sent to Hill Laboratories Limited, where they are oven dried at 62°C then ground to pass through a 1-mm sieve. Samples are analysed for F without washing, except for the split samples from sites 4, 5, 13, 18 and 19, which are washed prior to analysis. These five samples are acid detergent washed, as recommended by Mitchell (1986). Fluoride is then extracted in 0.1 M perchloric acid and measured with an ion-sensitive electrode. The detection limit is 2 mg F/kg.

A smart
green
future.
Together.