

# [Arsenic in ambient air](https://assignbuster.com/arsenic-in-ambient-air/)

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Executive Summary:

Ambient air in New Zealand has shown concerning amounts of speciated arsenic, especially in major cities like Christchurch. These heightened levels have been attributed towards the burning of CCA treated wood for household heating, being the main contributor to particulate arsenic concentrations in ambient air. In many cases, air samples showed levels of particulate arsenic that essentially surpassed the guideline concentration of 5. 5 ng/m 3 . Average concentrations of arsenic in Christchurch air samples were 5. 5 ng/m 3 for As(PM 2. 5 ) and 7. 1 ng/m 3 for As(PM 10 ). From this investigation, the collated data had shown very little information on long-term exposure and subsequent health effects related to particulate arsenic. From this, a recommendation was made to further pursue sampling and analyses of particulate matter in ambient air around Canterbury. Gathering in depth information on the health effects directly related to various airborne arsenic species.

Introduction:

Arsenic in ambient air has been a developing issue which has raised concern in New Zealand’s environment. The purpose of this report is to investigate the properties of airborne arsenic and recommend whether further sampling and research programmes should be implemented to gather sufficient data/statistics. This report will elaborate on arsenic sources in air, how it is measured and analysed, the toxicological effects with regards to human exposure and recommendations for further study.

Sources:
Arsenic (As) is an element that has been identified in over fifty different naturally occurring compounds throughout Earth’s environment. These can be found in water, crustal rock, soil, plants, animals, and air. 1, 2 However, it is most commonly found in the environment as inorganic arsenic, in the form of trivalent As(III) and pentavalent As(V) particulates in ambient air. 2, 3 Studies have shown that arsenic in this prevailing form has accredited for roughly 90% of total measured arsenic. 3 Organic arsenic is also present in much smaller quantities; the most common forms being dimethylarsinic acid (DMA) and monomethylarsonic acid (MMA). 2

It can enter the atmosphere by volcanic activity or through weathering of arsenic containing minerals. 4 Not only does arsenic appear in the environment through natural processes; it can also be released via anthropogenic activity. Mining and commercialisation of arsenic containing minerals, paired with industrial processes (fossil fuel combustion) accounts for the majority of arsenic dispersion in air. 4 In an industrial setting, arsenic typically forms as a by-product of smelting metal ores such as gold, lead, cobalt, zinc, and nickel. 4 Another source of arsenic includes treating timber specifically with chromated copper arsenate (CCA). This applies to New Zealand, especially in winter months, because treated timber is commonly sourced in urban areas for household heating. 5

Methods:

Sampling

Ambient air can be troublesome to analyse because of the complex combination of gas, liquid, and solid phase compounds. This can be problematic when measuring arsenic as an analyte, because it is susceptible to various analytical interferences. 3

A common sampling method includes using high volume air samplers fitted with particulate matter (PM) filters. Glass-fibre filters can be used as a sampling medium that is able to detect PM 10 sized particulates. Whatman quartz filters can be used to identify particulates that are PM 2. 5 sized. 6 These filters are preconditioned and weighed before sampling takes place. It may be required to measure the filters for background arsenic levels. Due to low concentrations of speciated arsenic in ambient air, similar concentrations within the sampling medium can be ruled out.

Analysis

Most analytical methods require air samples to be digested and extracted with acid before separation processes. 3 Using acids such as dichloromethane or water will produce two immiscible layers of extract in solution (organic and water soluble). 6 These extracts can then be fractionated and examined with analytical instrumentation.

The following methods are normally coupled with each other in order to lower detection limits and increase sensitivity, which improves the overall separation and analysis of arsenic species.

High-performance liquid chromatography (HPLC): A column chromatography based method which is able to fractionate and ascertain quantitative data. Analyte separation is dependent on polar character and interactions within the stationary phase of the column. 3 The ability to use various stationary and mobile phases particularly helps this technique to apply an extended range of separation mechanisms. This advantage allows HPLC to provide detailed data on speciation of the analyte. Hence why this technique is commonly used to separate species of soluble arsenic. 2

Hydride generation (HG): The analyte is converted into a volatile hydride, allowing species separation to occur. This technique has been regarded as a highly sensitive method, which specifically separates As(V) and As(III) when coupled with certain detectors. 3

Atomic fluorescence spectroscopy (AFS), atomic emission spectroscopy (AES), atomic absorption Spectroscopy (AAS): The analyte is exposed to electromagnetic radiation, causing the excitation of atoms. Different species can then be identified based on the difference in excitation energies. 3

Ion beam analysis (IBA): A process which involves the analyte being exposed to a high energy ion beam. Charged particles within the beam bombard the analyte causing the emission of particles from the sample in the form of radiation. 7 The radiation that is detected can be identified by observing different energies that are characteristic of certain species. These energies are evaluated and can be used to differentiate the speciation of the analyte. 7

Ion chromatography (IC): This analytical technique involves separation of polar molecules and ions based on the charge of the analyte. 3

Inductively couple plasma (ICP): The sample is passed through a nebuliser which converts the analyte into a fine mist of droplets. The aerosol is then introduced to a plasma torch and is vaporised. Excitation then causes atomisation of the sample. 8

Mass Spectrometry (MS): The analytes are converted into charged molecules from ionisation (molecular fragments of the analyte also occur). The charge to mass ratios of the ionised molecules are then measured. 3

Selected reaction monitoring (SRM): This technique can be incorporated in analytical processes that assess total arsenic (all species) in samples. Throughout preparation and analysis, verified standards of known concentration are maintained which allow the SRMs to recover accurate data on total arsenic. 3

Recent studies coupled HPLC, HG, and AFS/AAS/AES together in order to obtain a very sensitive analytical method, which was able to separate the following arsenic species from samples; As(V), As(III), DMA, and MMA. 3 Water soluble arsenic (higher bioavailability) can be obtained via analysis of water-soluble extracts, through atomic absorption spectrometry (AAS). 6 Other techniques commonly use ICP-MS in analysis. The overall efficacy of this method can be accredited to having highly specific and sensitive detection capabilities. 2

When measuring arsenic as an analyte, it is susceptible to various interferences including chemical, physical, and spectral, which impede analytical processes. Chemical interferences rarely occur in speciation analysis but can be influenced by ionisation effects, solute vaporisation effects, and molecular compound formation. 3 Spectral interferences can occur when determining the speciation of arsenic, particularly in ICP or AAS techniques. 3 Nonspecific absorption and light scattering can affect the analysis of arsenic in AAS. Isobaric intervention may transpire when using techniques that are coupled with ICP. 3 Another analytical issue, with regards to HG analysis, is the likelihood of producing arsine, which can be problematic for detection when other metals such as chromium, copper, and cobalt are present in high concentrations. 3 IBA typically has a higher limit of detection (LOD) compared to other analytical methods, being 20-30 ng/m 3 . 5 This can be problematic for detecting low concentrations of arsenic.

Taking a background correction (BGC) and the use of internal standards can be used to alleviate spectral interferences. Another solution to help prevent analytical interferences is adding EDTA to solution when extracting samples. Studies that applied this method observed exceptional levels of accuracy and control of interferences. 3

Previously Recorded Concentrations:

In New Zealand studies, most sampling methods took place over winter periods. This was based on the assumption that increased burning of CCA treated wood is the main contributor to particulate arsenic in ambient air.

A study was made on the biological effect of particulate matter and the chemical composition of ambient air particulates in New Zealand cities, including Christchurch and Auckland. Samples were collected from March to July in 2005. Results had shown that the average concentration for As (PM 2. 5 ) in ambient air (only measured in Christchurch) was 5. 5 ng/m 3 . 6 The average As(PM 10 ) concentrations for Christchurch was 8. 1 ng/m 3 . 6 These concentrations were much higher than ambient air samples taken in other New Zealand cities. This was most likely attributed to the increased use of wood burners for home heating in Christchurch.

When compared to other water-soluble metals, arsenic was present in relatively higher concentrations in both Auckland and Christchurch. It was assumed that particulate arsenic had a higher solubility compared to other metals in ambient air. 6

Although the study did not provide an annual statistic of the median concentration of water-soluble arsenic in ambient air, the median of samples collected in Christchurch showed to be noticeably higher than annual concentrations of water soluble arsenic in Edinburgh. The samples also showed to be higher than concentrations of total arsenic found in Spain, and five other cities located throughout Europe. 6

Another study that took place in Wainuiomata showed that the annual average of particulate arsenic concentrations (PM 10 ) in air was 7. 1 ng/m 3 between 1 Nov 2011 and 31 Oct 2012. 5

Human Toxicity:

Human exposure to particulate arsenic in ambient air ranges from 0. 4 to 30 ng/m 3 . 9 However, The Ministry for the Environment states that the annual average guideline for arsenic concentrations in ambient air is 5. 5 ng/m 3 , constructed from a one in one hundred thousand additional lifetime cancer risk. 5 Arsenic as well as arsenic containing compounds has also been classified by the International Agency for Research on Cancer (IARC) as a highly potent human carcinogen. 10

Compounds containing water soluble arsenic are easily absorbed when inhaled and ingested. Dermal contact can also prompt absorption of soluble arsenic. Health effects in extreme cases include bladder, lung, and skin cancer through ingestion and inhalation of arsenic containing compounds. 6

The 2005 study based in Christchurch and Auckland showed that ambient air samples collected in both cities during the winter period exhibited higher levels of mutagenicity, compared to the other seasons. 6 However, it can’t be assumed that the increase in mutagenicity levels are directly caused by PM related arsenic; only a correlation between the two is assumed.

Acute toxicity from short term exposure to arsenic includes abdominal pain, vomiting, and diarrhoea. Encumberment of muscles and the possibility of death can result from these symptoms. Long term toxicity from prolonged exposure to arsenic can drastically impact the physiology of humans. 10 Changes that are typically observed in dermal tissue include skin lesions, the alteration of skin pigments and hyperkeratosis. These symptoms normally develop after five years’ worth of arsenic exposure and can induce skin cancer. 10 The frequent burning and handling of CCA treated wood and ash disposal raises concern for acute arsenic toxicity, especially exposure via inhalation in homes that use wood burners for household heating in New Zealand. 5 Arsenic exposure directly from combustion is an unlikely scenario but studies show that the burning of CCA treated wood in a barbeque can induce acute arsenic poisoning [1] .

Other non-cancer endpoints from inhalation include nausea, respiratory irritation and neurological effects. Of the reported cases with these effects, all of them did not occur as frequently as cases that involved lung cancer. 3

In vitro studies have showed that toxicity is dependent on speciation of arsenic. Animal studies, for instance, have shown that As(III) exhibits a higher toxicity than that of As(V) in both cases of chronic and acute exposure to arsenic. [2, 10] It has been deduced that As(III) is roughly two to three times more toxic than As(V) in animals. 3 This degree of toxicity can also be extrapolated to human bio-toxicity.

Most studies have correlated health effects with accumulated data of total arsenic. However, exposure to arsenic in ambient air is dominated by interactions with arsenic that is bound to particulate matter, which raises uncertainty due to differences in speciation, bioavailability, and toxicity. 3

Although general trends show that inorganic forms of arsenic are generally more toxic, not enough research has been made on the toxicity and health effects of other arsenic species in ambient air. Another factor that determines arsenic toxicity is particle size. While accumulation of PM 10 and PM 2. 5 in the lungs can occur, PM 2. 5 is more likely to be toxicologically active due to the smaller size, allowing for particulates to be absorbed and enter the bloodstream. 3 Considering particulate matter, the frequent use of fossil fuelled technology and wood burning emissions leads to an increased toxicity of PM. 6

Although, symptoms may differ between individual people, due to different living environments and occupational conditions. The resulting paradigm is that there are no definite health effects, purely caused by direct contact with arsenic containing compounds. Direct exposure is unlikely to be long term and so is not regarded as a significant health risk. However, many of the symptoms described can be associated with biological interactions with arsenic containing compounds.

Conclusion:

To conclude, from the collation of data and information of various studies regarding air quality in New Zealand, observations of particulate arsenic in air have exceeded guideline concentrations on many occasions. Ambient air samples in Christchurch showed concentrations of 5. 5 ng/m 3 and 8. 1 ng/m 3 for As(PM 2. 5 ) and As(PM 10 ) respectively. The average arsenic in Wainuiomata also showed a reasonably high concentration of 7. 1 ng/m -3 of As(PM 10 ). These concentrations essentially exceeded the guideline of 5. 5 ng/m 3 , which may lead to potential health effects from acute and long term exposure. However, the severity of effects from particulate arsenic exposure may be negligible, since the toxicity of arsenic is determined by its speciation. Because various species co-exist in particulate matter, it can be problematic to determine the biotoxicity of total particulate arsenic.

A recommendation should be made for further research into the long term health effects, gathering an in depth understanding of direct impacts associated with prolonged exposure to arsenic in ambient air. A suggestion to make is to add more sampling units over a wider range of locations, with instrumentation that can sample various particle sizes. Overall, the inevitable solution to minimising particulate arsenic in ambient air is to prevent the combustion of CCA treated timber. In order to achieve this, government funding towards ‘ greener and cleaner’ methods of household heating could be implemented in Christchurch and potentially develop to a national level.

Calculations:

Assumptions made for calculations include the following:

That the annual amount of wood burnt is only done so during the winter period, with households requiring approximately ten cubic metres of wood as wood burner fuel 11 ; The type of wood used is only H4 grade CCA treated timber 1 ; Assuming that the wood is of the New Zealand Pinus Radiata species only and that wood density (550 kg/m 3 ) is maintained through treatment processes 12 ; soil density is 1. 3 t/m 3 ; no arsenic is lost through plant uptake or leaching; all ash from the wood burner is distributed evenly over the garden area.

Upper and lower limits of fireplace temperature have also been included. The lower limit being 22 percent of arsenic released at low temperatures (400 O C); the upper limit being 77 percent of arsenic released at high temperatures (800-1000 O C). 13

Inevitably, these calculations would only be representative of a “ worst case” scenario and most likely won’t correlate with true environmental values.

Amount of Arsenic in 100 kg of H4 treated CCA timber:

m(As) = m(wood) x (H4 As%)

–> 100 kg x 0. 0022 = 0. 22 kg

Total mass of wood:

m(wood) = V(volume) x P(density)

–> 10 m 3 x 550 kg/m 3 = 5500 kg of wood

Amount of arsenic in Wood:

m(As) = (H4 As%) x m(wood)

–> 0. 0022 x 5500 kg = 12. 1 kg

Amount of volatised arsenic:

m(As) volatile = m(AS) total x (As) released

m(As) Lower T = 12. 1 kg x 0. 22 = 2. 662kg/year = 2622 g/year

m(As) Upper T = 12. 1 kg x 0. 77 = 9. 317 kg/year = 9317 g/year

Total amount of ash:

m(ash) = m(As) total – m(As) volatile

m(ash) Lower T = 12. 1 kg – 2. 662 kg = 9. 438 kg = 9438000 mg

m(ash) Upper T = 12. 1 kg – 9. 317 kg = 2. 783 kg = 2783000 mg

Volume of soil:

V = area x height

V = 50 m 2 x 0. 01 m = 5 m 3

Total mass of soil:

m(soil) = V(volume) x P(density)

–> 5 m 3 x 1. 3 t/m 3 = 6. 5 t = 6500 kg

Arsenic concentration in soil:

[As] = m(ash) / m(soil)

[As] Lower T = 9438000 mg / 6500 kg = 1452 mg/kg

[As] Upper T = 2783000 mg / 6500 kg = 428. 2 mg/kg

Depending on the maximum heat output of the wood burner, a household can produce between 2622-9137 grams of volatised arsenic every year and arsenic concentrations in a garden fertilised with the resulting ash can range from 428. 2-1452 mg/kg.

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