

Appendix

The Flint water crisis (2014-2015)

In a cost saving initiative, beginning in 2014, the population of Flint, Michigan had their water supply shifted from Detroit's water system (Lake Huron) to the Flint River system, without assessing the safety of this new water source. The state of Michigan, having saved approximately \$7 million on the scheme, chose to ignore the deluge of complaints and reports from residents concerning the, at first, aesthetic quality of their potable water. It smelled of rotten eggs, tasted awful and was a muddy brown colour. This potable and agricultural water was in fact contaminated with lead, due to old leaded pipes being used in conjunction with the high corrosive nature of the Flint River system, as well as lack of anti-corrosives in said pipes. It was not until children began showing signs of lead's neurotoxic effects, contracting Legionnaire's disease; a severe form of pneumonia, that stakeholders were taken seriously – or rather more myopically, people in charge realised this would cost them far more than they had saved. 100,000 residents were then left without access to potable water, and 12 people or more died from the pollution. It has been argued that this is not only an example of irresponsible governance and planning but an outcome of deeper systemic racism and classism—due to the racial and economic makeup of the Flint community; >60% of Flint's population is comprised of persons of colour (POCs), and about 40% lived below the poverty line. Lead concentration upwards of 397 parts per billion (ppb) were measured, with the US EPA listing a maximum safe level of 15 ppb. The \$7 million the state saved on the scheme turned into a \$626 million settlement paid out to the affected children, families and businesses of Flint who had paid for a service they did not receive (BBC, 2021).



Top: A local child holding up a jar of lead tainted water at one of many protests which took place between 2014-2016. Bottom: A comparison between water from the Flint system and the Detroit system -which was used prior to 2014.

Arsenic pollution in Bangladesh and east India

A well-known case of As toxicity arising from non-anthropogenic sources but due to anthropogenic activity comes from Bangladesh and eastern India. In the 1970s, residents of these areas were encouraged to pump groundwater from the Ganges-Brahmaputra-Meghna Delta due to bacterial contamination of surface waters and the, often true, assumption that groundwater would be safer as it is more protected from surface pollution. This was a project by UNICEF and the World Bank, with the intention of meeting safe water drinking goals. Groundwater had already been used as a source for irrigation. Tens of thousands new wells, assumed and intended to be safer than the polluted surface waters, led to grave ecotoxicological consequences in the 20-30 million residents, currently at 50 million, who

began using groundwater for domestic purposes (vanLoon and Duffy, 2011); slowly but surely poisoning an entire nation. Already in the 1980s, patients began presenting with skin lesions which, in the worst of cases, devolve to cancer, cardiovascular disease, and other illnesses. An estimated 40,000 people die of arsenic poisoning each year in Bangladesh. Arsenic is highly insoluble and found in trace amounts within the Delta in the form of arsenides associated with sulphide minerals. The actual source is not yet understood but hypotheses exist. These include: the oxidation of minerals leading to release of arsenate and arsenite into water due to reduction in groundwater levels, the reduction of Fe_2O_3 minerals sorbed to arsenic which undergo reduction in anoxic organic-matter rich sediments, and fertiliser derived phosphates dislocating arsenite and arsenate from sorped sites (vanLoon and Duffy, 2011). As the true cause of As pollution is not yet known, preventative efforts have been difficult to establish. Presentative efforts have therefore been focused on establishing the safety of individual wells, as wells vary greatly in arsenic concentrations, by distinguishing them via markings (Photograph X).

A survey conducted in ?? measured As in groundwater from “64 districts in the country and found that 59 had concentrations $>10\mu\text{g L}^{-1}$ and 43 had concentrations $>50\mu\text{g L}^{-1}$ ” (Hosseini, 2006, p.1). The safe concentration of As in drinking water according to the WHO is $10\mu\text{g L}^{-1}$. Some 97% of the population in Bangladesh rely on groundwater as a potable water source.



A Bangladeshi person with hyperpigmentation on their left hand, and the loss of two fingers on the right due

to arsenic damage (Rafiqur Rahman for Reuters, 2015)



Top Left: A well designated as safe by the colour green. Top Right: A Bangladeshi person carrying a marking designating a well as unsafe using the colour red. Bottom: An overview map of safe and unsafe wells.

itai-itai disease, Japan

The name of this disease translates from Japanese to “it hurts-it hurts”; the words spoken by patients arriving at hospitals in agony. It resulted from pollution of the Jinzu River Basin in Toyama prefecture, Japan. The source was an upstream zinc mine named Kamioka mine,

operated by the Mitsuni mining and smelting company (Kaji, 2012). The first cases, not yet understood, appeared in the early 1900s and it was not until the 1960s that Cd pollution of rice paddies was identified as the source. Cd often appears in minor quantities in Zn deposits and as such is a byproduct of Zn mining. Between 1910-2007 ca.400 people, have been affected. The disease causes severe bone pain, fractures, pseudo fractures (Looser's zone) and renal tubular dysfunction. The bulk of those affected were women, likely due to their lower bone mass density and weight.



Photograph X. Child suffering from itai-itai disease, presenting with change in bone structure. Original source unknown. Adapted from Dökmeci and Ongen (2009).

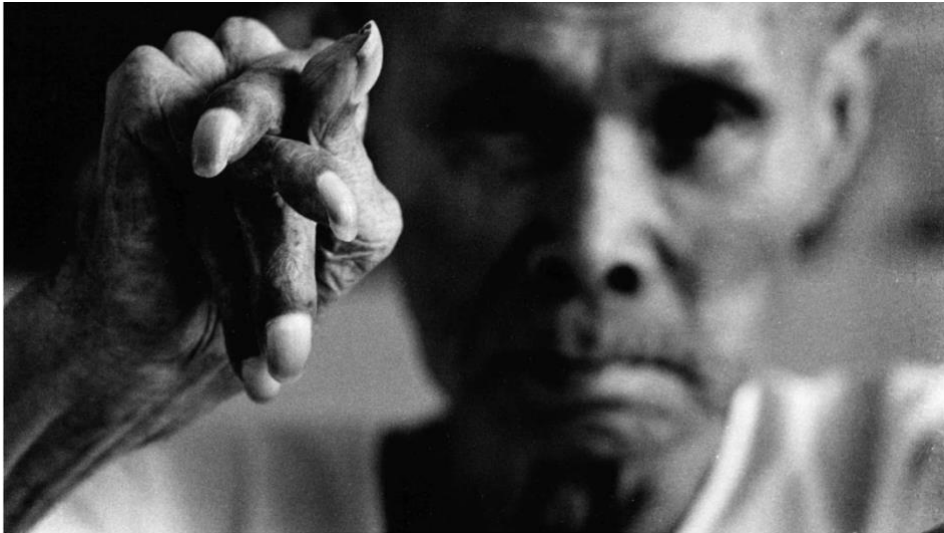
Minamata Bay disease, Kumamoto and Niigata prefectures, Japan

In the city of Minamata within the Kumamoto prefecture in Japan, locals began showing symptoms of a central nervous system disease in 1956 (Ishikawa and Ikegaki, 1980). A second disaster occurred in 1965, dubbed the second Minamata Bay disease, or Niigata Minamata disease where locals surrounding the Agano river in the Niigata prefecture were subjected to the consequences of mercury-containing industrial wastewater being dumped into the river (Ishikawa and Ikegaki, 1980). The company responsible was in 1968 found to be the Chisso Company; renamed Japan New Chisso (JNC) in 2012. The source was the release of organic methylmercury due to inorganic mercury's use as a catalyst in the production of acetaldehyde at the plant. The dumped industrial waste containing bioavailable and neurotoxic organic mercury accumulated first in shellfish and fish through absorption by

skin or gills and up the trophic scale until it reached the human population, which was heavily reliant on fish protein. Some 100 people lost their lives as a result, with many becoming disabled (Walker et al., 2012). The impact of both these disasters was exacerbated by the affected population's dependence on fish as their primary source of protein. Populations with a low diversity in diet are less resilient and more at risk from such catastrophic events (Walker et al., 2012). Today there are approximately 3000 humans recognised as victims of Minamata disease. A depressing fact is that governmental acknowledgment of the disease's source came in 1968, the year an economically viable alternative to mercury in acetaldehyde production became available.

According to the Minamata disease museum's website the symptoms include *“numbness and unsteadiness in the legs and hands, tiredness, ringing in the ears, narrowing of the field of vision, loss of hearing, slurred speech, and awkward movements. Some early severe victims of Minamata disease went insane, became unconscious, and died within a month of the onset of the disease.*

There are also victims with chronic Minamata disease symptoms, such as headaches, frequent tiredness, loss of the senses of smell and taste, and forgetfulness, which are not easily visible but make daily life difficult. Moreover, there are congenital Minamata disease patients, who were born with handicaps after being attacked by methyl mercury while in the wombs of their mothers who consumed polluted fish. No cure for Minamata disease has yet been discovered, so treatment consists of attempts to lessen the symptoms and physical rehabilitation therapy. In addition to the physical damage, there is also social harm, such as discrimination in relation to Minamata disease.”



Photograph X. Iwazo Funaba, a person with Minamata Disease, taken 10 years after its onset. Photograph by Shisei Kuwabara, 1970.



Photograph X. Tomoko, a victim of Minamata disease, celebrating her "Coming of Age Day" with her father. Photograph by Shisei Kuwabara, 1977.

Thallium



Photographs X. Left: 42-year-old patient presenting with infected acneform lesions, lip oedema, and angular stomatitis on day 13 of illness. Right: Alopecia on day 45 of illness. While many signs and symptoms of thallium poisoning may be conflated with those of arsenic poisoning, alopecia is highly indicative of the former (Misra et al., 2003) Thallium poisoning should also be considered in patients presenting with rapidly progressing peripheral neuropathy (nerve damage), regardless of whether alopecia is present (Rusyniak et al., 2002).



Photograph X. Patient presenting with erosion of proximal parts of nails following thallium poisoning (Saha and Sadhu, 2004).

Testing of physical and chemical parameters

Testing methods for some physical and chemical parameters are provided below, as well as brief discussion of these parameters. These are sourced from the DIN spec, as well as Krogstad and Børresen's Field and Laboratory Methods (2015) and a write-up to videos

handed in for fulfilment of GEO220.

Dry matter (DM)

Method : drying

Dry amples are first sieved, spread out onto a tray and placed in a drying cabinet overnight at 35-40°C to hinder microbial activity tampering with the sample before dry matter content determination. Next, 5g samples are weighed into porcelain crucibles –which must also be weighed but tend to be ca. 20g is heated at 105°C for 24 hours. Samples are then cooled and weighed. %DM is found by dividing sample weight before drying by sample weight after drying.

Organic Dry Matter (ODM)

Method: loss on ignition (incineration/calcination)

5%DM

Loss on ignition is a method for estimating organic matter content in samples. It is obtained by first straining samples through a 2mm sieve. Special ceramic bowls are then weighed both with and without a sample (often 5g) to obtain the weight of the sample before drying. Samples are then heated at 105°C for a minimum of 6 hours, after which they are weighed once more. The loss here is water-weight. This needs to be corrected based on clay content, as it is assumed that in clayey samples water is bound more strongly and may not be lost entirely upon heating. Next, samples are heated at 550° C for a minimum of 10 hours - keeping in mind that it takes about an hour to heat up the oven, and weighed again. Loss on ignition is then obtained as a percentage of loss on ignition.

Loss on ignition ensures that samples are rid of organic matter, as well as chemically bound water. It is found by weighing out 5g samples of fertiliser into porcelain crucibles (20mg?) and placing them into a calcination oven. Samples are heated at 550°C for 3 hours, allowed to cool and weighed once more. Loss on ignition is then calculated in % by dividing the decrease in weight of dried sample after calcination by the weight of dry sample before calcination. To comply with requirements presented in the spec, ODM must make up no more than 5% of DM.

Salt content/ Conductivity (in KCl/g):

Method: Conductivity meter in H₂O eluate

Threshold 0,5g/l

Conductivity is a measure of the ability to transmit an electrical current. Truly pure water is an insulator. The more ions we measure, the higher its conductivity. This will depend on the concentration of ions, their valence and mobility. Conductivity is an indicator of water's source. While rainwater has a conductivity of about 10µSiemens, groundwater -with its high content of dissolved minerals- tends to be much higher. Conductivity is affected by temperature and is ideally measured at 25C. A conductimeter -the instrument we use to measure conductivity- can correct for temperature variations.

pH

pH, from the latin for power and quantity of hydrogen, is operationally defined as the negative logarithm of the hydrogen ion concentration $-\log(\text{H}^+)$. It ranges from 0 to 14, where 7 is neutral. The more H⁺ ions we measure, the lower the pH of (or the more acidic) a solution is. The more hydroxide ions OH⁻ we have, and thereby the less H⁺ ions, the higher the pH and more basic/alkaline it is. There is an inverse relationship between these two. At the neutral pH of 7, their concentrations are equal. It is worth noting, however, that their values are higher than zero, as deprotonation of water molecules will still naturally occur.

A logarithmic scale is used due to the wide range of concentrations we may measure. This tells us that if we have a sample with a pH of 5, for example, and another with a pH of 6 there is a difference of one order of magnitude between the two (by a factor of 10). The sample with a pH of 5 has 10 times more H⁺ in it than the one with a pH of 6; and consequently 10 times less OH⁻ ions. A sample with a pH of 5 would then have a 1000x higher H⁺ concentration compared with one with a pH of 8.

PH is technically based on H⁺ and hydroxide ion *activities*, as opposed to concentrations. This is because ions in a solution interact, which can affect measurements giving false concentration values. While the definition of pH we are familiar with may be true for highly diluted solutions, it is incorrect for samples with a high ionic content. Calibrating the pH

scale against concentration is difficult, and results in an approximation. It is therefore, operationally, the effective activity of ions we measure when we measure pH. To make things easier, and obtain comparable results, the pH of samples is conventionally measured by calibrating instruments against buffer solutions with known pH values. Calibration is a vital step prior to measurement.

pH affects the solubility of pollutants and metals, thereby affecting their toxicity, and whether or not they will be transported long distances or become bioavailable, eventually accumulating in organisms and up the trophic scale. It also affects the availability of macro and micro plant-nutrients, which have varying ideal pH ranges depending on their charge, size and other properties. There are varying availabilities of plant nutrients at different pH. Soil with a pH of 7.5 is considered alkaline, and 8 very alkaline; while that with a pH of 5 is acidic, and pH of 4 is very acidic.

In order to measure pH, 10ml samples are placed in a graduated beaker with 25ml deionized water and sealed with a lid, after which they are thoroughly shaken and left to sediment. They are mixed once more and left to settle for 15 minutes. A pH meter is calibrated against two buffers at pH 4 and 7 and a standard buffer with a known pH (e.g., 6.87). The meter is made up of a calomel electrode and a glass electrode leaking potassium chloride (KCl) covered in a permeable H⁺ sensitive glass membrane. These are placed within samples and pH values are noted once they stabilise.

Even though the spec does not specify this, CaCl₂ is more reflective of plant experience when fertilised, as introducing some salts increases H⁺ in the solution (McCauley et al., ??). The author recommends testing in CaCl₂ as well as deionised water. This leads to a pH value which is lower by 0.5-0.9 pH units. On the other hand, the electrode itself leaks KCl, a salt, and may compensate somewhat for the naturally occurring salt content in soils (Prasad and Power, 1997). According to the spec, all pH values are to be labelled.

Alkaline active ingredients /alkalinity (CaO)

Alkalinity is a measure of ability to neutralise acids, it gives an idea of a media's resistance to changes in pH -it is its buffering capacity; its resilience. The higher the mineral content, the more alkalinity is a measure of carbonate and bicarbonate content. In waters with low mineral contents, for example, alkalinity is mostly provided by other basic materials such as humus.

To measure alkalinity we need to titrate. Titration is a process whereby an acid with a known concentration is added to the sample until a particular pH is reached. This means we need to measure pH (Section X) while we titrate. Samples are titrated down to a pH of 4.5. At this pH it is assumed that all bicarbonates (HCO_3^-) have been converted to carbonic acid (H_2CO_3), or to put it in other words -that the buffering capacity has been “used up” in samples with pH lower than 8.3. In samples with a pH greater than 8.3, where hydroxides also contribute to the buffering capacity, carbonates (CO_3^{2-}) are titrated to bicarbonates at pH 8.3 and to carbonic acid at pH 4.5.

Method

Dissolved samples with measured volumes are titrated against HCl down to pH 4.5. The volume of titrant is noted, alongside the HCl concentration and used to calculate alkalinity using the following formula, where C is concentration and V is volume:

$$\text{Total alkalinity (mmol/l)} = (C_{\text{HCl}} * V_{\text{HCl}} * 100) / V_{\text{sample}}$$

According to the spec, the threshold for alkaline active ingredients is 5% of dry matter content.

Phosphate (P₂O₅)

Extraction in aqua regia (a mixture of nitric and hydrochloric acid in a molar ratio of 1: 3) and atomic emission spectrometry (ICP-OES) There are two acknowledged methods for determination of phosphate content, these are digestion in aqua regia (a mixture of nitric and hydrochloric acid in a molar ratio of 1: 3) under reflux conditions or using a microwave, or followed by ICP-MS or ICP-OES; or via addition of molybdate and determination using spectrophotometry at 880nm. The former is recommended for measurement in the DIN spec, while the latter follows the recommended standard [NS-EN-ISO-6878](#) in the norwegian "forurensningsforskriften" (ref).

Heavy metals (As, Pb, Cd, Cr, Cr(VI), Cu, Ni, Hg, Tl, Zn);

Heavy metals have been discussed in (Sections X). When ionised they are cations; positively charged ions and can therefore be measured using Inductively coupled plasma optical emission spectrometry (ICP-OES) per the spec requirements. The noble gas argon (Ar) is introduced into a chamber and ionised to plasma by heating to 1000K (726,85 °C; 1340,33 °F). Samples are sequentially introduced into the chamber as a fine aerosol mist and

the influx of energy causes electrons in their outer orbital to "jump" up an energy level/orbital. This is a cascade effect, whereby atoms "crash" into one-another leading to a chain reaction of ionisation. Upon reaching cooler areas of the chamber these electrons jump down an energy level and that additional energy is emitted in the form of light (photons) at specific wavelengths. Various measured wavelengths are then compared against standards to determine both concentration and species of cations. An issue which might arise here is that some metals may have very similar wavelengths. In the spec, all heavy metals are measured in this way; the exception being chromium (VI). Cr (VI) is measured through extraction in demineralised water and photometric determination of Cr (VI) 1,5 diphenyl carbazide.