

# SEWAGE TREATMENT

Sewage is a mixture of domestic and industrial wastes. It is more than 99% water, but the remainder contains some ions, suspended solids and harmful bacteria that must be removed before the water is released into the sea.

The treatment of wastewater is divided into three phases: pretreatment, primary treatment and secondary treatment.

## **Pretreatment**

Large solids (i.e. those with a diameter of more than 2cm) and grit (heavy solids) are removed by screening. These are disposed of in landfills.

## **Primary treatment**

The water is left to stand so that solids can sink to the bottom and oil and grease can rise to the surface. The solids are scraped off the bottom and the scum is washed off with water jets. These two substances are combined to form sludge.

## **Secondary treatment**

The sludge is further treated in 'sludge digesters': large heated tanks in which its chemical decomposition is catalysed by microorganisms. The sludge is largely converted to 'biogas', a mixture of CH<sub>4</sub> and CO<sub>2</sub>, which is used to generate electricity for the plant.

The liquid is treated by bacteria which break down the organic matter remaining in solution. It is then sent to oxidation ponds where heterotrophic bacteria continue the breakdown of the organics and solar UV light destroys the harmful bacteria.

## **The role of the laboratory**

A wide variety of analytical tests are used to determine the purity of the wastewater at various stages of treatment so that the possibility of harm to either people or the environment is minimised.

## INTRODUCTION

Sewage is a major carrier of disease (from human wastes) and toxins (from industrial wastes). The safe treatment of sewage is thus crucial to the health of any community. This article focuses on the complex physical and biological treatments used to render sewage both biologically and chemically harmless.

The Auckland region has two sewage treatment plants: one in Albany and one in Mangere. The process described below is that used by the Mangere treatment plant, which was built in 1960 and currently serves Auckland, Manukau and Waitakere Cities and the Papakura District. It is the largest such treatment plant in New Zealand, but its methods are similar to those used throughout the country.

The waste treated is a mixture of domestic and industrial waste, with the domestic accounting for

slightly more than half of the total. Some stormwater also enters the system through leaks and illegal connections<sup>1</sup>.

### **Volume and composition**

On average, 280 000 m<sup>3</sup> of sewage arrives each day, although during winter storms this can swell to 800 000 m<sup>3</sup>. Of this, 99.9% is water. The remainder is mostly organic matter (800 - 1000 g m<sup>-3</sup>) which constitutes the bulk of the suspended solids (250 - 400 g m<sup>-3</sup>). The biological processes which break down this organic matter require oxygen, and the amount of oxygen required is calculated as the wastewater's "biochemical oxygen demand" (BOD). Sewage coming into the plant (influent) has a BOD of between 200 and 400 g m<sup>-3</sup> (i.e. 200 to 400 grams of oxygen are required to oxidise each cubic metre of influent). The remaining organic matter consists of the fat and grease that form a scum on the surface of the influent.

As well as organic matter, small amounts of inorganic ions are also found. The most significant of these are chloride (100 - 200 g m<sup>-3</sup>) and sulphide (0.1 - 0.7 g m<sup>-3</sup>). Sulphide, despite its low concentration, is of greater concern than chloride because it is very foul-smelling even at this level.

The influent generally contains no dissolved oxygen, so this must be added at various stages of the process to enable the organics to be broken down.

## **THE TREATMENT PROCESS**

The purification works at Mangere provide both primary and secondary treatment processes. Primary treatment removes most of the solids from the effluent, but doesn't remove or degrade the dissolved organic matter. Secondary treatment uses microorganisms to convert these organics to simple compounds, and uses the energy of the sun to destroy pathogens<sup>2</sup>. The effluent is then safe to be discharged into the Manukau Harbour. The entire process is shown diagrammatically in **Figure 1**.

The works have been designed to take advantage of the natural features of the site. Oxidation ponds provide very economical secondary treatment and these were chosen because a suitable area of harbour mudflats could be formed into ponds and because Auckland has the sunny climate necessary for the efficient working of the ponds.

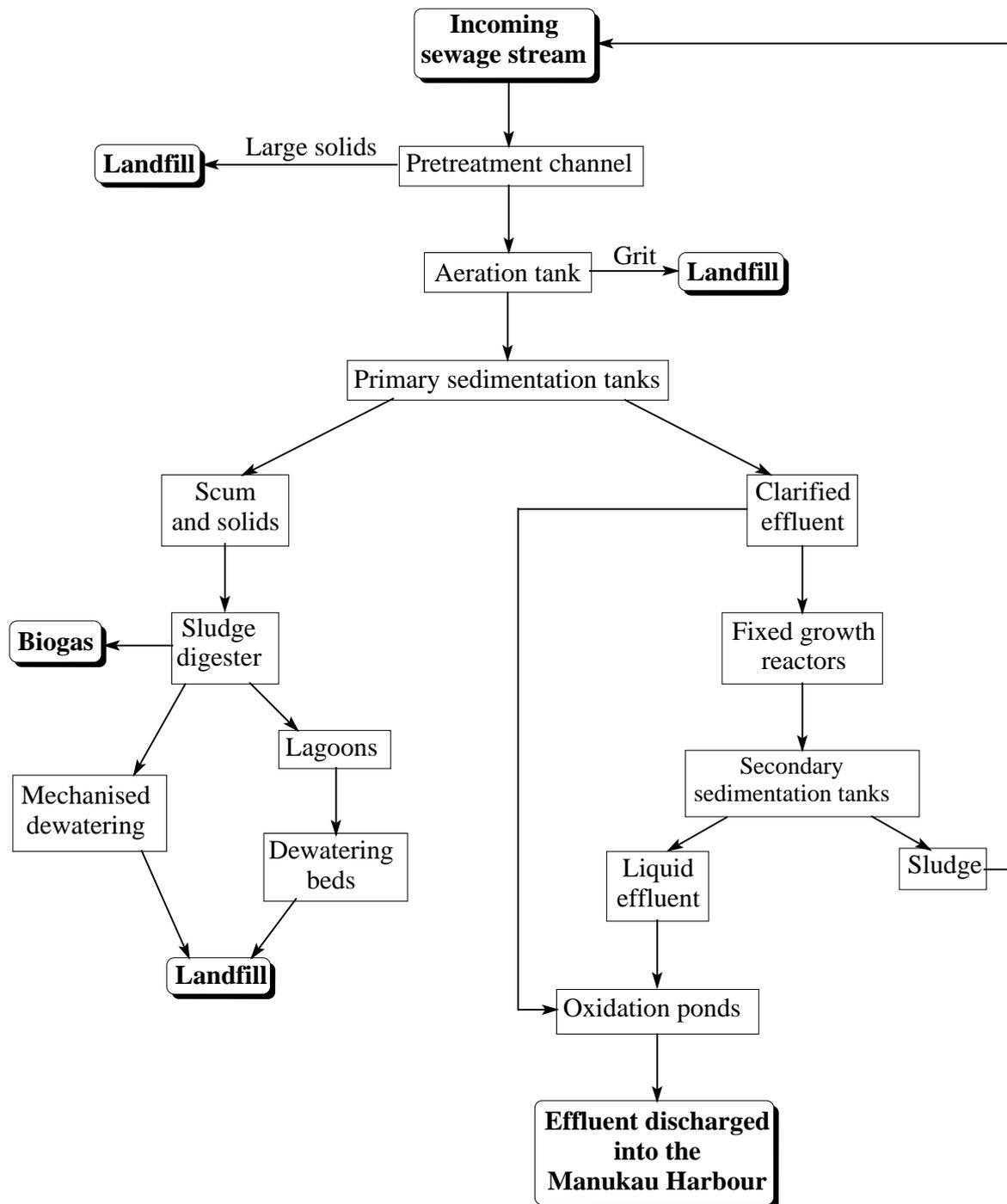
Conditions in the ponds promote the growth of unicellular algae: minute plants which, like any other plants, absorb carbon dioxide in daylight and give off oxygen by photosynthesis. This oxygen oxidises the organics, thus purifying the sewage by reducing its oxygen demand. The ponds absorb an amount of solar energy equivalent to a 745 kW engine running continuously. Such engines are in fact required by other modern sewage treatment processes where the works must be restricted to a smaller area.

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<sup>1</sup>Most of Auckland's stormwater is collected in a separate stormwater collection system and either discharged directly to the harbours or treated in settling ponds. Part of Auckland City has a combined sewage and stormwater system, but this system has a limited capacity and during heavy rain overflows of combined stormwater and sewage can occur.

<sup>2</sup>Disease-causing bacteria

**Table 1** lists the various treatment tanks and ponds in the order that they are mentioned below, while **Table 2** describes the treatment of the various effluent streams separated out of the incoming wastewater.



**Figure 1 - Sewage treatment flow diagram**

### Step 1 - Pretreatment

Pretreatment removes the large solids (such as rags and sticks) that are carried in with the wastewater. These are removed by screens consisting of metal bars spaced at 19 mm intervals which are placed across the influent channels. Tines (metal combs) rake the collected matter off these, and heavy objects such as rocks (which would otherwise damage the equipment) are

allowed to sink into a hopper. The remaining solids are dewatered using a compacting screw and then collected for landfilling off site. About 6 m<sup>3</sup> of large solid matter is collected this way each day.

**Table 1 - Treatment equipment**

Item	Number	Combined capacity	Residence time
Pretreatment channels	4	12,000 L s <sup>-1</sup>	Negligible
Pre-aeration tanks	12	9274 m <sup>3</sup>	30 minutes
Primary sedimentation tanks	12	28224 m <sup>3</sup>	2 - 3 hours
Sludge digesters	7	52150 m <sup>3</sup>	20 days
Sludge lagoons	6	3 m deep each	3 - 4 years
Dewatering beds	6	200,000 m <sup>2</sup>	1 year
FGRs	4	88250 m <sup>3</sup> (wheel surface area is 4 800 000 m <sup>2</sup> )	
Secondary sedimentation tanks	4	19 600 m <sup>3</sup>	2 - 3 hours
Oxidation ponds	4	6 750 000 m <sup>3</sup>	25 days

**Table 2 - Treatment of removed material**

Substance removed	Volume	Treatment
Pretreatment screenings	6 m <sup>3</sup> / day	Compacted then landfilled
Grit	3.4 m <sup>3</sup> / day	Washed then landfilled
Sludge and scum	2000 m <sup>3</sup> / day	Digested then landfilled
CH <sub>4</sub> and CO <sub>2</sub>	500 m <sup>3</sup> / tonne of solids	Burnt as fuel
Sludge filtrate	86.5% of incoming sludge	Returned to incoming wastewater

## Step 2 - Primary Treatment

Here grit (fine, hard solids), suspended solids and scum are removed in two stages.

### *Preaeration*

Firstly the wastewater is aerated by air pumped through perforated pipes near the floor of the tanks. This aeration makes the water less dense, causing the grit to settle out. As the air jets are positioned such that the water is swirling as it moves down the tanks the suspended solids are prevented from settling out. The air also provides dissolved oxygen for the bacteria to use later in the process, but the wastewater is not in these tanks long enough for bacterial action to occur here. The grit is collected in hoppers and washed, after which it is used for on site land reclamation and landscaping.

### *Sedimentation*

The water then flows slowly and smoothly through the sedimentation tanks, where the suspended solids fall to the bottom and scum rises to the surface, while clarified effluent passes on. The solids are removed from the bottom of the tanks by scrapers, and scum is washed off with water jets. The scum and solids are brought to a common collection point where they are combined to form 'sludge' and sent off for secondary treatment.

### **Step 3 - Secondary Treatment**

After secondary treatment all effluent, both solid and liquid, is sufficiently safe to be released into the environment. The treatment of solids and liquids are covered separately below.

#### *Solids*

Sludge from the sedimentation tanks is digested anaerobically in large tanks, and then further digested in lagoons before being dried in dewatering beds. In the sludge digesters the sludge is kept at 37°C and mechanically mixed to ensure optimum operation. During this time the organic compounds within the sludge are converted to carboxylic acids and then finally to methane and carbon dioxide. This gaseous mix is known as "biogas", and is a valuable source of fuel. At Mangere it is used to generate electricity, which is primarily used to drive the plant machinery, with any excess electricity being sold to Mercury Energy. The exhaust created by burning the biogas is used to heat the sludge in the digesters.

When the sludge leaves the digesters it has undergone a 50% volume reduction. It is then sent to lagoons for about a year, and finally to dewatering beds. During this time all pathogens are killed by the sunlight.

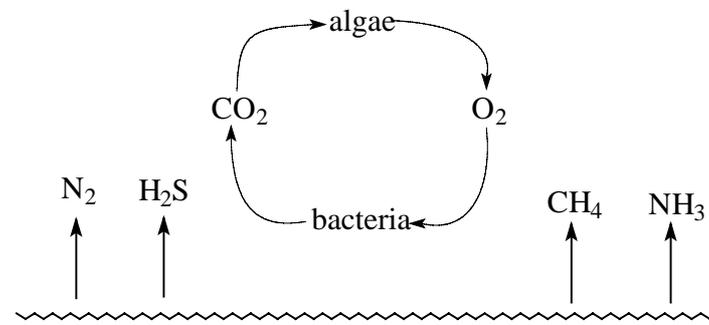
A small proportion of the sludge is currently mechanically dewatered instead of being treated in the lagoons and dewatering beds. Polyelectrolytes are added to the sludge, and the attraction of opposite charges causes a floc (loose aggregation of particles) to form. Most of the water is then removed by rollers squeezing the mixture. After this the sludge has become concentrated from 4 to 30% solids, and could potentially be used as a soil conditioner, although currently it is simply landfilled.

#### *Liquids*

The liquids are either sent directly to open-air oxidation ponds, or sent to 'fixed growth reactors' to reduce their BOD before pond oxidation. The fixed growth reactors (FGR's) are tall, circular tanks covered with fibreglass. Each one is filled with approximately 36 million 10 cm diameter PVC 'wheels'. Microorganisms live on the wheels, and these reduce the BOD of the sewage by a further 75%. The wastewater is sprayed on the top of the wheels and percolates down, with the organics being reduced to CO<sub>2</sub>, CH<sub>4</sub> and a small amount of foul-smelling H<sub>2</sub>S. From the bottom of the FGR the effluent is piped to one of the secondary sedimentation tanks where sludge (consisting mainly of dead microorganisms from the FGR's) is removed. This sludge is piped back to join the incoming wastewater and complete the cycle again.

The wastewater then joins the liquid that was sent straight to the ponds for oxidation, where an influent mix of primary and secondary treated wastewater and some recycled pondwater is received. The mix is precisely calculated to ensure that the amount of organics entering the pond is the optimum amount for the bacteria to process given the amount of oxygen available at that time.

A diagram of the processes taking place in the ponds is given in **Figure 2**. The effluent entering the ponds is a mixture of primary and secondary treated effluent, with the relative proportions varying during the year. During summer the pond algae produce large amounts of O<sub>2</sub> by photosynthesis, so the proportion of effluent that has only been primary treated (i.e. the proportion that requires large amounts of O<sub>2</sub>) is greater, whereas in winter more secondary treated effluent is used.



**Figure 2 - Reactions occurring in the oxidation ponds**

In the pond, algae use solar energy to produce oxygen from carbon dioxide and water, and bacteria use oxygen to break down the remaining organics to simple molecules such as carbon dioxide and ammonia. The sun also destroys pathogenic bacteria, while the wind ensures even mixing so that all parts of the ponds are aerobic.

This treated effluent is then released into the Manukau Harbour at each high tide.

## THE ROLE OF THE LABORATORY

The laboratory carries out a significant range of tests at various stages of the treatment process to ensure effluent purity and to protect water and equipment at other stages of the process. Many of these tests can only be used to monitor a single parameter, but a small number have much wider application. These are:

- Atomic absorption spectroscopy (AA), which is used to detect the presence of many metals.
- Inductively coupled plasma (ICP), also used to detect metals. Together these techniques can be used to monitor all the metals of interest in wastewater.
- Gas Chromatography (GC), which is used to detect certain organic species.

Specific tests are used to monitor a wide variety of substances, conglomerations of substances and more general properties of the wastewater. Substances monitored are:

- Elements (phosphorous and nitrogen)
- Molecules (ammonia and dissolved oxygen)
- Ions (nitrite, nitrate and sulphide)

In addition, some conglomerations of substances (which include many individual chemical species) are monitored:

- Solids content (both suspended and total)
- Oil and grease (which includes anything that can dissolve in the solvent used)

And finally, some parameters of the solution as a whole are tested for:

- pH
- Alkalinity
- BOD5 (the amount of oxygen consumed by biological degradation processes over a five day period)
- COD (the amount of oxygen required to completely oxidise the chemical species present)
- Turbidity

There are different test frequencies for different sample sites. Tests such as BOD and suspended solids are usually carried out frequently, e.g. daily or weekly, while other tests such as those for metals are done only occasionally, e.g. monthly or quarterly. The tests are discussed individually below.

### Atomic absorption spectroscopy (AA)

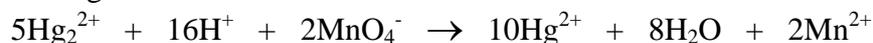
Atomic absorption spectroscopy involves atomising a sample, and measuring the absorption of light passing through the vapour containing the atoms of the element, the amount of light absorbed depending on the amount of element present in the vapour. Specific lamps emitting light of frequency absorbed by the element are required for each element. There are two techniques used in wastewater treatment to atomise the sample: Flame AA and Cold vapour AA.

#### *Flame AA*

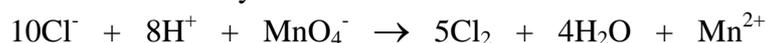
This technique is used for detecting cadmium, chromium, copper, lead, silver and zinc, (see **Table 3**). The sample is fed into a high temperature flame, causing it to split up into its individual atoms. The light from the specific lamp passes through the flame containing the element and a detector measures the light intensity of the light emerging. This technique determines whether the element is present, and its concentration.

#### *Cold vapour AA*

Mercury is the only metal that is liquid at room temperature. For this reason, its atomic absorption spectrum can be determined simply by collecting its vapour (as all liquids have vapour above them) and directing a light beam at this. As mercury is found in ionic rather than metallic form in wastewater it first has to be reduced to its metallic form. This is done in three steps. First, the sample is treated with a strong oxidising agent (a mixture of  $\text{KMnO}_4$ ,  $\text{K}_2\text{S}_2\text{O}_8$  and  $\text{HNO}_3$ ). This removes many of the substances that could interfere in the test, and also oxidises  $\text{Hg}_2^{2+}$  to  $\text{Hg}^{2+}$ :



Unfortunately, this also oxidises any chloride to chlorine:



This is a problem because  $\text{Cl}_2(\text{g})$  absorbs light of 253 nm, which is very close to 253.65 nm, the absorbance frequency of  $\text{Hg}(\text{g})$ . For this reason, the second step involves sparging<sup>3</sup> the solution with  $\text{N}_2$  gas to remove the  $\text{Cl}_2$ .

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<sup>3</sup>Sparging involves bubbling an inert gas through a solution to remove any gas dissolved in that solution. It works because as the inert gas is bubbled through, the proportion of the dissolved gas in the vapour above the liquid decreases so more gas must come out of solution to maintain equilibrium. Eventually this results in effectively all of the dissolved gas being removed.

The mercury II is then reduced to metallic mercury using stannous chloride:



The mercury is then removed from solution by sparging with helium. The mercury is then swept by the helium to an absorbance cell where a light beam is directed through it to establish whether or not any mercury was present in the original sample.

**Table 3 - Atomic absorption and emission frequencies of metals in wastewater**

<b>Metal</b>	<b>Absorption frequency / nm</b>	<b>Absorption detection limit / ppb</b>	<b>Emission frequency / nm</b>	<b>Emission detection limit / ppb</b>
<b>Arsenic</b>	—	—	193.76	2
<b>Cadmium</b>	228.80	1	226.50	0.05
<b>Chromium</b>	357.87	3	205.55	0.009
<b>Copper</b>	324.75	1	327.40	0.006
<b>Lead</b>	283.31	240	220.353	0.6
<b>Mercury</b>	253.65	0.02 <sup>4</sup>	—	—
<b>Silver</b>	328.07	1	328.07	0.8
<b>Zinc</b>	213.86	1	202.55	0.6

### **Inductively coupled plasma (ICP)**

This is another technique in which a metal is atomised, but this time the light it emits (rather than the light it absorbs) is measured. In ICP the sample is atomised by being injected into a chamber filled with an argon plasma<sup>5</sup>. The plasma is of sufficient energy to atomise the sample and excite electrons to higher energy levels. The light emission spectrum of the excited free atoms is measured. Arsenic, cadmium, chromium, copper, lead, silver and zinc (and many other metals not found in sewage) each have a characteristic emission band (**Table 3**) and can be detected in this way.

### **Gas chromatography (GC)**

This technique is used for determining many different organic compounds, and is based on the fact that different organic compounds bind to the same polymer with different binding strengths. The sample is injected into a narrow tube which is packed with polymer beads (the nature of the polymer depends on the substance being analysed). The tube itself is coiled up inside an oven and heated to up to 400°C. The temperature used depends on the substance being analysed.

<sup>4</sup>This is when cold vapour AA is used. With flame AA the detection limit is 140 ppb.

<sup>5</sup>A plasma is an ionised gas - in the case of argon, a mixture of Ar<sup>+</sup> and e<sup>-</sup>. Overall a plasma is uncharged, but it is made up of charged particles. A huge amount of energy is required to create and sustain a plasma, and in ICP this energy is provided by a high frequency electric field which is produced by an induction coil.

The heat of the oven causes the organic compounds of interest to be volatilised, and this gas is carried through the tube by an inert gas<sup>6</sup>. As it passes along, substances which bind strongly to the beads will progress slowly, whereas ones which are only weakly bound to the beads move much more quickly - in this way the different substances are separated out. At the end of the tube a detector measures the time of elution and amount of each gas fraction as it appears.

Acid herbicides (i.e. 2,4-D and 2,4,5-T), PCBs and organochlorine pesticides are all measured in this way. Volatile organic compounds are measured using a slightly more sophisticated version of gas chromatography known as GC-MS.

### **Gas chromatography - mass spectroscopy (GC-MS)**

This technique is used to separate out a mixture of compounds collectively known as 'volatile organic compounds'. There are many compounds in this group, including such substances as benzene, carbon tetrachloride, toluene and 1,1,1-trichloroethane.

The gaseous mixture is extracted from solution by sparging with an inert gas. The organics thus driven off are adsorbed onto a 'sorbent trap' - a tube packed with beads of silica gel and a 2,6-diphenylene oxide polymer and beads coated with methyl silicone. This trap is then heated and a backflow of inert gas desorbs the gases and carries them into a GC column. They progress through the column as described above, but this time each fraction coming out of the column is sent to a mass spectrometer. In the mass spectrometer molecules of the compound are ionised and some of the positively charged ions dissociate into smaller fragments. The spectrometer separates the ions, gives their mass to charge ratio, and the relative amount of each ion. Compounds have distinct mass spectra. This gives two parameters by which each compound can be identified - the time of elution from the column and its mass spectrum. As before, the read-out from the GC column itself also gives the amount of that compound was present.

### **Total phosphorous**

Phosphorous is present in wastewater almost solely as phosphates, which come from three main sources - cleaning solutions, fertilizers and biological wastes. It is an essential nutrient for most organisms so its must be removed from wastewater to prevent the growth of harmful bacteria.

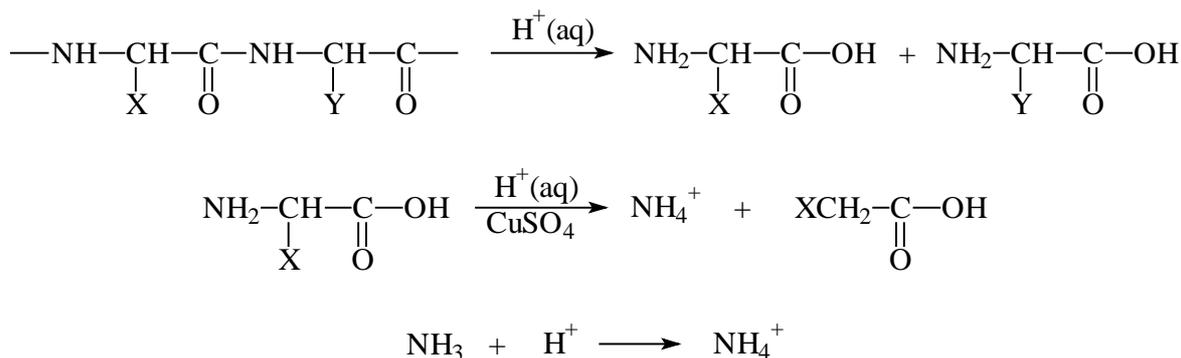
Phosphorous levels are measured colorimetrically by converting the phosphorous to a highly coloured complex known as 'molybdenum blue'. The first step in this process is to oxidise all the different phosphates up to orthophosphate ( $\text{PO}_4^{3-}$ ) using a 1:5 mixture of  $\text{H}_2\text{SO}_4$  and  $\text{HNO}_3$ . This orthophosphate is then reacted with ammonium molybdate and potassium antimonyl tartrate in the presence of acid to give a yellow complex which is then reduced with ascorbic acid to molybdenum blue. The intensity of the blue colour can be measured and compared with a standard calibration curve to determine the exact amount of phosphorous present in the original sample.

### **Total organic nitrogen**

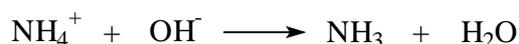
The term 'organic nitrogen' refers to nitrogen from proteins, free amino acids and ammonia, and excludes nitrogen from nitrite and nitrate ions. The amount of nitrogen present in a sample is determined by heating it in acid with a copper sulphate catalyst until it has all been converted to  $\text{NH}_4^+$  ions:

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<sup>6</sup>In this case an inert gas is one which does not bind to the beads in the tube



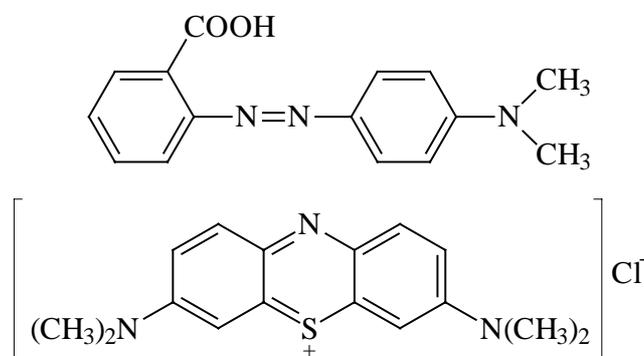
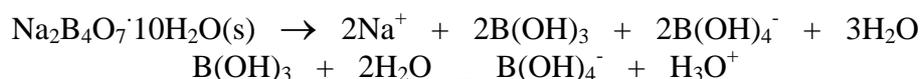
The ammonium ions are then converted with base to ammonia:



And the quantity of ammonia is determined using the method described below.

### Ammonia (NH<sub>3</sub>)

Very low concentrations of ammonia (i.e. less than  $2.9 \times 10^{-5} \text{ mol L}^{-1}$ ) are determined using an autoanalyser with colorimetric detection. Any higher concentrations are determined by titration against H<sub>2</sub>SO<sub>4</sub>. The titration is done by adding a borate buffer to the solution to keep it at pH 9.2 (to prevent hydrolysis of cyanates and organic nitrogen to NH<sub>3</sub>) and then distilling off the NH<sub>3</sub>. This is titrated against H<sub>2</sub>SO<sub>4</sub> using a combined indicator of methyl red ( $pK_a = 5.0$ ) and methylene blue.



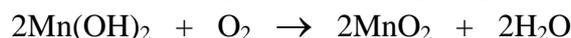
### Dissolved oxygen (O<sub>2</sub>)

This is determined by two methods. One uses an "oxygen selective" electrode and is an electrochemical method which can be taken out of the laboratory. The other is based on the Winkler chemical method which involves a series of ionic and redox reactions which result in the formation of iodine at a concentration proportional to the initial concentration of dissolved oxygen in the sample. The amount of iodine is then determined using a redox titration. Dissolved oxygen is essential for any aerobic biochemical activity to occur, thus its levels are a useful indicator of biochemical activity.

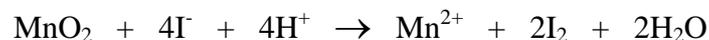
The process involves dissolving MnSO<sub>4</sub>, NaOH and NaI in the sample to be tested. These are then involved in a series of reactions. Firstly, a manganese hydroxide precipitate forms:



This is then oxidised by the dissolved oxygen to a  $\text{MnO}_2$  precipitate:



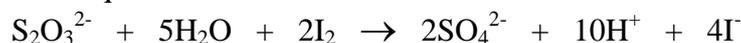
The solution is then acidified to dissolve the precipitate so that it can react with the iodide in solution to form iodine:



Thus overall the manganese has simply acted as an oxygen carrier, and the reaction occurring has been:



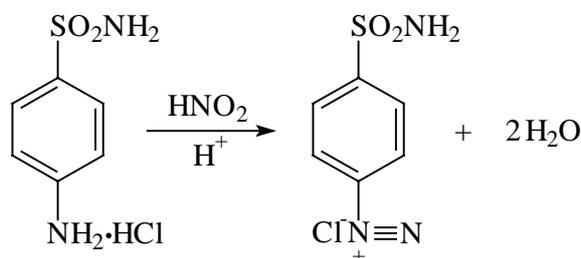
The concentration of the iodine is then determined by titration with  $\text{Na}_2\text{S}_2\text{O}_3$ . Before titration the solution is yellow-brown (the colour of aqueous iodine). When this colour is almost too pale to be detected, a small amount of starch is added because starch forms a dark blue-black complex with iodine. When the blue-black colour disappears, end-point has been reached. It is much easier to see when the starch complex has disappeared than to see when the pale straw colour of the iodine is gone. The equation for this redox titration is:



Thus  $1\text{O}_2 = 4\text{I}_2 = 2\text{S}_2\text{O}_3^{2-}$

### Nitrite ( $\text{NO}_2^-$ )

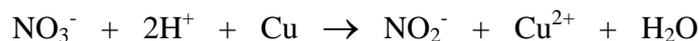
Nitrite is determined by Griess-Ilosvay's method. This involves reacting the nitrite with sulphanilamide to form a diazonium compound:

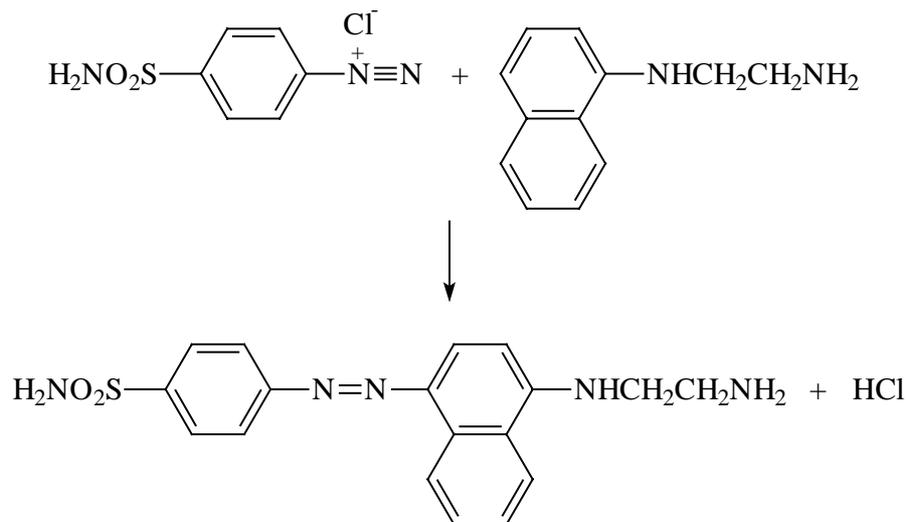


The diazonium compound reacts with N-(1-naphthyl)ethylenediamine as shown in **Figure 3** to form a highly coloured azo dye which can be determined spectrophotometrically.

### Nitrate ( $\text{NO}_3^-$ )

The amount of nitrate is determined by measuring the amount of nitrite in a sample, reducing the nitrate to nitrite, measuring the nitrite again and calculating the difference. The nitrite is determined using the method described above, and the nitrate is reduced to nitrite with copper in a Cu/Cd column:

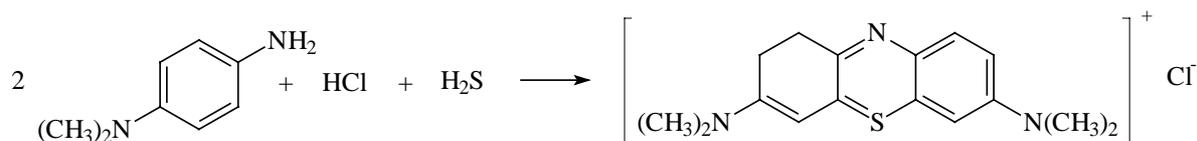




**Figure 3 - Coupling reaction of the diazonium ion to form an azo dye**

### Sulphide ( $S^{2-}$ )

$H_2S$  and N,N-dimethyl-*p*-phenylene diamine react to form methylene blue (a strongly coloured complex) in the presence of  $FeCl_3$ :



The concentration of  $S^{2-}$  is determined by preparing two solutions of wastewater and iron chloride. To one is added the amine, while to the other methylene blue is added dropwise until the intensity of colour in both solutions is identical. The number of moles of sulphide is equal to the number of moles of methylene blue added to the second solution.

### Suspended solids

These are determined in a purely physical process: the solution is filtered through a weighed glass fibre disk, the disk is dried in a desiccator and the weight increase measured.

### Total solids

This measurement is also done in a physical process. Here the sample is placed in a weighed dish in an oven at between  $103^{\circ}C$  and  $105^{\circ}C$ . The dish is weighed periodically until the weight becomes constant. The difference between this weight and the weight of the dish is the total weight of solids.

### Oil and grease

The sample concerned is acidified to pH 2 (to prevent oxidation) and mixed in a separating funnel with a weighed amount of solvent (an 80:20 mixture of *n*-hexane and methyl-*t*-butyl ether). The two solutions are shaken together so that any oil or grease present in the aqueous phase can migrate to the solvent phase, in which it is more soluble. After thorough mixing the water (lower layer) is drained off and any solids and remaining water are separated from

the solvent by filtering it through anhydrous  $\text{Na}_2\text{SO}_4$  (which absorbs water) on filter paper. The solvent is then weighed, with the weight increase being due to the oil and grease.

The category 'oil and grease' is intended to include triglycerides and the long chain hydrocarbons and complex aromatics and naphthenes of mineral oils. However the solvent used also dissolves sulfur, simple aromatics, short-chain hydrocarbons and chlorophyll. As 'oil and grease' is defined in this context as anything that dissolves in the above solvent mixture, for this purpose all of these substances are considered to be oil and grease.

## pH

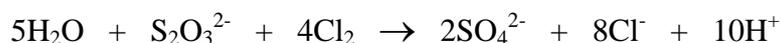
pH is a measure of the concentration of  $\text{H}_3\text{O}^+$  ions in the solution. It is measured using an ion-sensitive electrode known as a glass electrode.

## Alkalinity

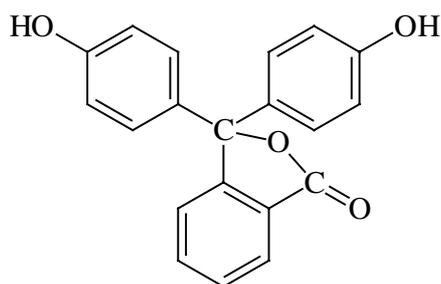
Alkalinity differs from pH in that alkalinity is a measure of how much acid is required to neutralise a solution, which takes into account not only the pH but also whether or not a buffer is in operation. The buffer that one expects in wastewater is the carbonate buffer, a mixture of  $\text{CO}_3^{2-}$  and  $\text{HCO}_3^-$ . The solution is then titrated with a strong mineral acid — either  $\text{H}_2\text{SO}_4$  or  $\text{HCl}$ , using the indicators phenolphthalein ( $\text{pK}_a = 9.6$ ) and bromocresol green ( $\text{pK}_a = 4.7$ ).



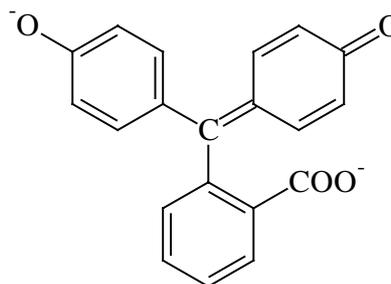
Before titration for alkalinity of the wastewater  $\text{Cl}_2$  present must be destroyed, as it could interfere with the second end point. This is done with thiosulphate:



The first endpoint is reached when all the  $\text{CO}_3^{2-}$  has been converted to  $\text{HCO}_3^-$ , and all  $\text{OH}^-$  has been converted to  $\text{H}_2\text{O}$ . This occurs at pH 8.3, at which time the phenolphthalein changes from red to colourless:

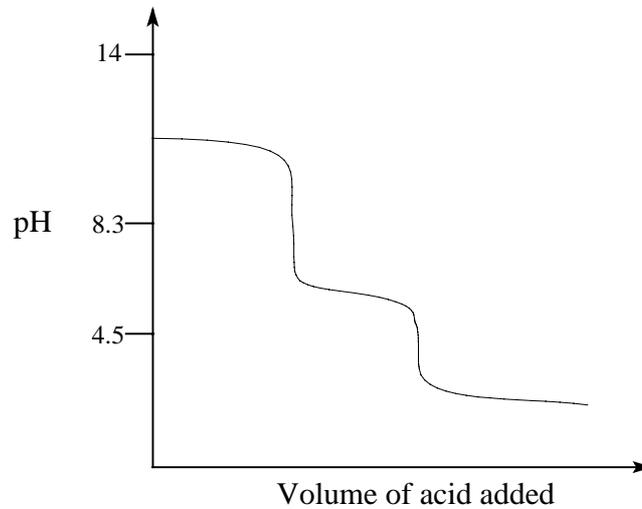


**phenolphthalein - acid form**



**phenolphthalein -base form**

At this point bromocresol green is added, turning the solution blue. As more acid is added, the indicator turns yellow, indicating that the pH is now 4.5 and the second end-point has been reached. The number of moles of acid needed to reach the first end-point is the number of moles of carbonate and hydroxide ions (combined) present in the original solution, while the number of moles of acid needed to go on to the second end-point is the combined number of moles of carbonate and bicarbonate ions present in the original solution. As the amount of hydroxide ions present is usually very small, subtracting the first number from the second number gives a relatively accurate figure for the amount of bicarbonate ions originally present. **Figure 4** shows the titration curve obtained during this titration.



**Figure 4 - Carbonate titration curve**

**Five day biological oxygen demand (BOD5)**

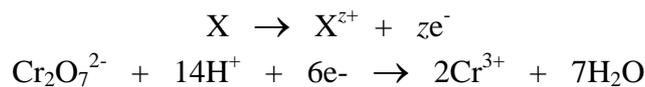
The 'strength' of sewage is defined as its biological oxygen demand (BOD) - the amount of oxygen required for biochemical oxidation of the sample. The BOD is proportional to the amount of organic matter in the sample. Normally, the BOD is calculated as a BOD5 - the consumption of dissolved oxygen over a five day period. This is done by measuring the amount of oxygen present in a diluted sample (diluted such that a reading of approximately 2 mg L<sup>-1</sup> O<sub>2</sub> is obtained as the technique is most accurate around this range), incubating it in sterile conditions for five days at 20 ± 1°C and again measuring the dissolved oxygen content. The total BOD of the sewage at the plant is about 83 000 kg/day.

This technique is complicated by the fact that inorganic nitrogen can also be oxidised under these conditions. As this technique is intended to only measure the oxygen demand of the organic material in the sample, allyl thiourea is added to the incubating material to prevent the oxidation of these compounds.

**Chemical oxygen demand (COD)**

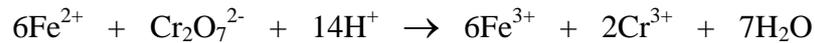
Whereas the BOD of the sewage is a measurement of the oxidation that actually occurs in the sewage due to biochemical degradation, the COD is a measure of the total quantity of oxidisable material in the sample. It is measured using a strong oxidant (potassium dichromate) and determining the extent to which that oxidant has been consumed.

The first step is to acidify the solution and add a known but excess amount of dichromate. Any reduced substances are oxidised and a proportionate amount of the dichromate is reduced:



Some dichromate is left unreacted. The second step is to determine the quantity of this by a redox titration. Ferrous ammonium sulphate - Fe(NH<sub>4</sub>)<sub>2</sub>(SO<sub>4</sub>)<sub>2</sub> · 6H<sub>2</sub>O - is added to the solution, as well as a small quantity of a "Ferrouin" indicator. The Fe<sup>2+</sup> is oxidised by the

dichromate, and end-point is reached when no dichromate is left to react with the iron. The redox reaction occurring is the following:



An empirical relationship between chemical oxygen demand and biological oxygen demand can usually be determined, and hence a COD measurement can be used to determine the accuracy of a BOD measurement. A BOD measurement is of more practical use as it is the BOD which determines the impact a sample would have on the environment.

### **Turbidity**

Turbidity is a measure of the cloudiness of the water, which is due to the presence of fine colloidal and suspended matter such as clays and microorganisms. It is measured using a physical technique known as nephelometry: the measurement of the scattering of light as it bounces off particles in solution. It is a simple technique, in which a light beam is directed at a sample and the light intensity is measured at 90° from the beam's initial angle.

## **ENVIRONMENTAL IMPLICATIONS**

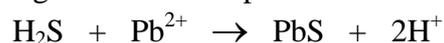
### **Odour control**

In the absence of adequate oxygen bacteria in the wastewater break down essentially odour-free compounds to odorous compounds: fats and carbohydrates go to alcohols, esters, aldehydes and carboxylic acids while proteins go to ammonia, amides, mercaptans and hydrogen sulphide. All of these compounds can give off strong smells, but those formed from protein degradation can emit very intense smells at concentrations in the parts per billion range.

The foul air containing these compounds is mostly formed in the pretreatment and primary treatment phases. For this reason, the equipment used in these phases, as well as the fixed growth reactors and the sludge dewatering plant, are roofed over and the gases produced in these areas are removed using extractor fans. They are piped to one of six 'earth filters': mounds of soil and finely ground sand and scoria with a total surface area of 9800 m<sup>2</sup> and an average total depth of 1m. The air is released from perforated pipes underneath the soil and percolates upwards. Organisms convert sulfurous compounds to sulfur, nitrogenous ones to nitrogen and organics to CO<sub>2</sub> and CH<sub>4</sub>.

### *Odour monitoring*

The upper acceptable limit for H<sub>2</sub>S is 5 ppb. To ensure that the H<sub>2</sub>S concentration does not rise above this level on the borders of the treatment plant, a 'chemcassette' monitoring system is used. In this a tape impregnated with lead acetate is exposed to the air for 15 minutes. If H<sub>2</sub>S is present then the following reaction takes place:



The darkness of the lead sulphide on the tape is compared with a standard response curve to determine the ambient H<sub>2</sub>S levels.

Other odours are measured using a trained panel of 'sniffers': people who monitor whether a particular gas is detectable by smell and whether it is present at offensive levels.

### Effluent quality

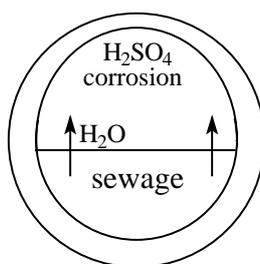
Watercare is required to meet strict effluent quality guidelines, which primarily control the level of pathogens and the BOD of the effluent released into the harbour. However, even though the effluent meets these guidelines it is considered unsafe to collect shellfish near the effluent discharge point. With the new plant (see below) the effluent will have an even higher purity, and the restricted area will be further reduced.

### Pipe corrosion

H<sub>2</sub>S causes significant problems in sewer pipes. It is a potent poison and must be monitored in all pipes to ensure that levels are low before Watercare staff enter the pipes for inspection. However a further and less well known consequence of the presence of H<sub>2</sub>S in pipes is pipe corrosion. Anaerobic bacteria in the sewage feed on the amino acids and release H<sub>2</sub>S. This then dissolves in the water on ceiling of the pipe, where other, aerobic, bacteria use it as a source of energy:



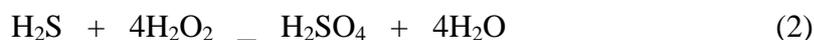
The sulfuric acid thus produced corrodes the upper surface of the sewerage pipes, regardless of what material they are made of. **Figure 5** illustrates the process.



**Figure 5 - Sewerage pipe corrosion**

In Australia, rates of corrosion of concrete sewer pipes of 0.25 inches per annum in problem areas are not unusual, and the only real solution available to control the problem is to use very thick layers of concrete and to inspect pipes regularly.

Some sewage treatment plants are using hydrogen peroxide to deal with the sulphide problem. Dissolved sulphides are oxidised to elemental sulphur and/or sulphate.



Reaction (2) occurs in alkaline solutions (pH>9) and SO<sub>4</sub><sup>2-</sup> and H<sub>2</sub>O are the major products. Lime and bleaching powder can be used to ensure the correct alkalinity and reduce microorganism levels.

## THE FUTURE OF WASTEWATER TREATMENT IN AUCKLAND

In 1993 it was decided that a new wastewater treatment facility was needed for Auckland because:

- The population is expected to grow by at least 25% over the next 25 years.

- Nutrient and pathogen levels in released effluent are currently too high (currently 10 tonnes of nutrients, mostly in the form of green algae, are released into the harbour each day).
- Odour and midges cause a significant annoyance to local residents.

For these reasons a new plant is gradually being built, to be completed in 2003. This will involve two major changes:

- Sludge will be removed in an 'activated sludge unit' (incorporating the dewatering plant described above). This means that the BOD will be reduced by more than 50%, nitrogen levels by at least 75% and suspended solids by 70%. Sludge lagoons and dewatering ponds will gradually be removed. The more efficient removal of organic matter means that around 30% more sludge will be produced in the new system.
- The oxidation ponds will also be removed as they will no longer be needed for reducing the BOD of effluent. To kill the pathogens that are currently destroyed in the oxidation ponds the effluent will be irradiated with UV light.

These changes will result in a much higher quality effluent, and largely remove the current odour and midge problems.

This original article of the first edition has been revised for this edition by Heather Wansbrough and John Packer following a visit to the Mangere sewage treatment plant. Information compiled with assistance from Gladys Balmer, Claire Jackman and Peter Raines (Watercare) and with reference to:

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- Clesceri, Leonore S., Eaton, Andrew D. and Greenberg, Arnold E. (eds); *Standard Methods for the Examination of Water and Wastewater (19th edition)*; American Public Health Association, American Water Works Association and Water Environment Federation; 1995
- Townshend, Alan; *Encyclopedia of Analytical Science*; Academic Press; 1995