Groundwater Contamination Due to Irrigation of Treated Sewage Effluent in the Werribee Delta

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ABSTRACT: The Werribee River, groundwater and Melbourne's treated sewage effluent (or recycled water) are used for irrigation water in the Werribee Delta. Groundwater beneath the Werribee delta may be contaminated by the recycled water. The mixing ratios of the sea water, upstream groundwater and recycled waters for delta groundwater were calculated from water chemistry. The mixing ratio of the recycled water varied from 10 to 30 % at all depths and delta groundwater was found to be largely comprised by irrigated recycled water. The NO_3^- contamination of delta groundwater is thought to be caused by recycled water and agricultural use of fertilizers. A high mixing ratio of sea water was found at 30 m in depth and this zone was thought to be a salt-water wedge.

Keywords: Recycled water, Sewage irrigation, Estimation, Groundwater origin, Metal contamination

1. INTRODUCTION

1.1 Study area and Purpose

The Werribee delta area is 30 km west of Melbourne, Victoria, Australia (Fig.1). The delta is important for growing vegetables for the city of Melbourne, but because of low precipitation (average 500 mm per year [1]), irrigation is required for adequate production purposes, with Werribee River, delta groundwater and more recently treated sewerage waters (recycled water) all having been used for irrigation. Groundwater in the delta area is pumped up from 6 to 30 m in depth. In 2003, a 2 m decline in the aquifer level, and increasing salinity (as measured by a change in electrical conductivity (EC)from 2,500 to 9,000 $\mu S\ cm^{-1}$) led to bans and restrictions on ground water use [1]. In 2004, the use of recycled water from Melbourne's Western Treatment Plant began. Approximately 90 % of the irrigators had signed on to receive recycled water by 2008. Although the average salinity of the recycled water is 2,000 $\mu S\ cm^{-1}$ and is less than groundwater EC, groundwater contamination caused by irrigation water is a concern for both irrigators and environmental managers because the recycled water contains trace elements and high nitrogen concentrations. In this study, the origin of the groundwater was estimated using water chemistry, including stable isotopes, and the influence of recycled water on groundwater was clarified.

1.2 Recharge area

The upper catchment of the Werribee area consists of Silurian sandstone and mudstone, Devonian granite, Permian glacial tillite, older Tertiary basalt and recent alluvial sand; the middle stream area consists of Pliocene basalt; and the lower stream area consists of recent alluvial sediments [2]. The basement of the middle to lower stream area is Tertiary sediment covered with basalt lava and recent alluvial sediments [3]. The Tertiary sediments are composed of sand, clay and gravel including older volcanics and have high water permeability. Prior to this study, the recharge area of delta groundwater was thought to be in the middle and lower catchment to delta area.

2. METHOD

2.1 Sampling and analytical method

Sea, river, borehole, recycled and rain waters were studied between 2,007 and 2,010. Sea water was sampled at the delta coast. Borehole waters were sampled from the mid catchment area to the delta area. The Werribee River and its surrounding river waters were sampled along their courses. Recycled waters were sampled from irrigation supply channels and drains in the delta. Rain water was sampled at Werribee city. Temperature, pH, ORP and EC values were measured on site using a portable instrument (HORIBA, pH meter D-54, 55). Samples for anion and cation analysis were filtered through 0.45 μm filters and were measured using liquid ion chromatography (DIONEX, DX-ICS, AQ-1,500 and ICS-1,600). Also HCO_3^- was measured by an acidic titration. Trace elements in the samples were analyzed by ICP-MS (Ultramass ICP-MS, Varian Australia). The oxygen and hydrogen stable isotope ratios of water samples were measured using a mass spectrometric system (Finnigan Mat Delta Plus), followed by the CO_2-H_2O and H_2-H_2O equilibration technique using platinum catalyst. The measured oxygen isotopic ratio was calculated using equation (1).

$$\sigma(\text{per mil}) = (R_x / R_{st} - 1) \times 1{,}000 \qquad (1)$$

where R_x is the stable isotopic ratio of x, sample and R_{st} the stable isotopic ratio of st, standard.

2.2 Sample points

The Werribee River waters were classified into three zones based on catchment topographic features (Table 1). Specifically, river delta sites were on the Werribee River less than 20 km from the coast; river medium sites were mid-catchment locations on the Werribee River 20 to 40 km from the coast; river upstream sites were on the Werribee River 50 to 60 km from the coast. The river water samples include a small number of the samples collected from tributaries of the Werribee River (the Lerderderg River,
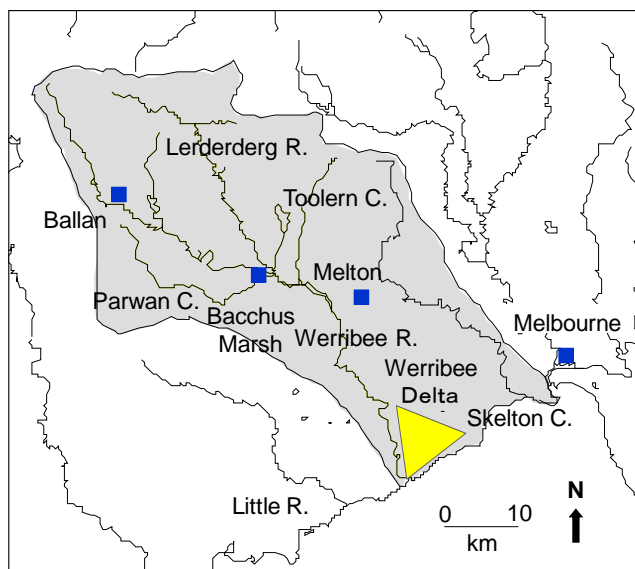
Fig.1 Werribee River catchment

Parwan Creek, and Toolern Creek (excluding the lower stream area)) and the rivers bordering the Werribee delta on its west and eastern sides (Little River, and Skelton Creek) (Fig.1).

Groundwater was sampled from borehole. Boreholes were also classified according to catchment location: borehole delta sites were in the Werribee Delta area in an area intensively irrigated by recycled water less than 10 km from the coast; borehole medium sites were in the lower catchment of the Werribee River around the delta 10 to 20 km from the coast; borehole upstream sites were in the middle catchment of the Werribee River 20 to 40km from the coast.

Sea water was sampled in Port Philip Bay and the Werribee River estuary.

Table 1 Sampled points from the Werribee catchment area

| Sampled water	Distance from coast	Character
River delta (Werribee River)	Less than 20 km	Delta and plain, lower catchment
River medium (Werribee River)	20 to 40 km	Plain, middle catchment
River upstream (Werribee River)	50 to 60 km	Mountain, upper catchment
Borehole delta (groundwater)	Less than 10 km	Werribee Delta, intensive irrigation, lower catchment
Borehole medium (groundwater)	10 to 20 km	Plain, agriculture, lower catchment
Borehole upstream (groundwater)	20 to 40 km	Plain, agriculture, middle catchment

3. RESULTS and DISCUSSION

3.1 Character of water chemistry for sea, groundwater, recycled water and rivers

Since 2,004, recycled water has used for irrigation in the Werribee Delta and by 2,006, over 80 % of the irrigation water was recycled water. Consequently, the Werribee Delta groundwater, borehole delta water was thought to be

derived from four components, recycled water and river water from surface, sea water from sea side, borehole medium water as upstream groundwater.

Not surprisingly, Cl^- concentrations were extremely high in sea water relative to all river waters sampled (Fig.2). Specifically, the sea water had an extremely high concentration of Cl^- (above 20,000 mg/l outside of the estuary) relative to the recycled water (average 450 mg/l), the borehole medium (average 1,400 mg/l), and borehole upstream (average 400 mg/l); Cl^- concentrations in river water increased upstream to downstream from 90 to 1,200 mg/l. Generally, dissolved Cl^- is stable and not adsorbed by soil and so Cl^- is a good indicator of the mixing ratio of sea water. Cl^- concentrations in borehole delta samples were on average 1,400 mg/l, the same as those of borehole medium water but extremely high values were included. So, some borehole delta water was thought to contain sea water through underground flow (intrusion) of sea water into the delta area.

Typically, NO_3^- and PO_4^{3-} concentrations in sewage water are high because sewage water contains a myriad of N- and P- containing organic compounds. Two ions, NO_3^- and PO_4^{3-}, were thought to be good indicators for recycled water; this turned out not to be the case. For instance, although NO_3^- concentrations for the recycled water were high (average 65 mg/l), the borehole delta water had an average NO_3^- concentration of 70 mg/l, with many samples having NO_3^- concentrations higher than those of recycled water (Fig.3). River, sea and borehole medium and borehole upstream water NO_3^- concentrations were very low (Fig.3), so the higher NO_3^- concentration for the borehole delta waters was thought, at least in part, to be derived from fertilizer use in this intensively farmed area. Similarly, although PO_4^{3-} concentrations in the recycled water were very high (average10 mg/l), PO_4^{3-}
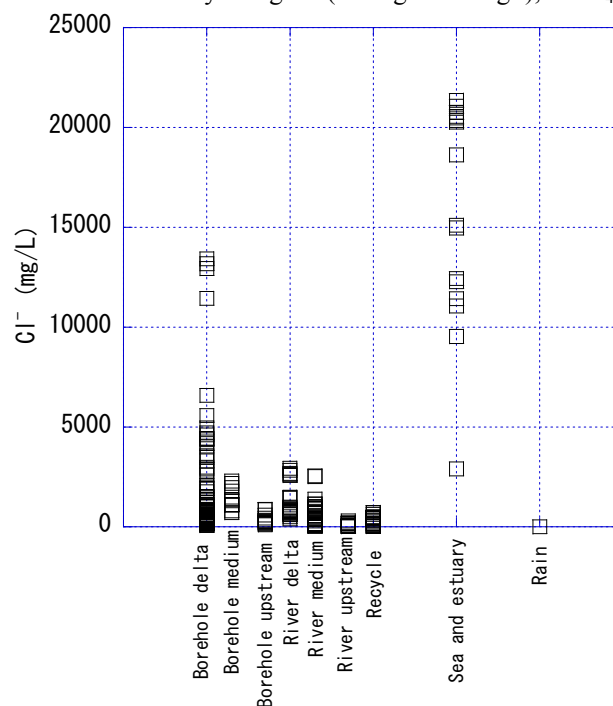
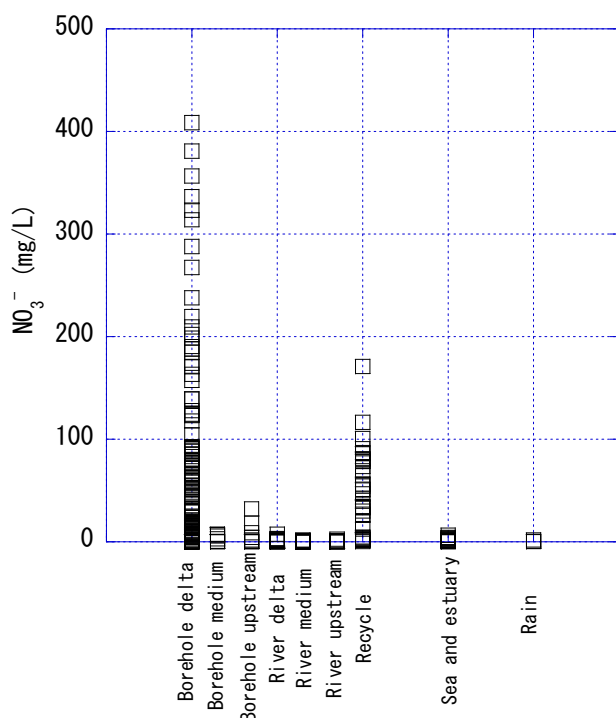Fig.2 Cl^- concentrations in sea water, groundwater, recycled water and rivers

Fig.3 NO_3^- concentrations in sea water, groundwater, recycled water and rivers

Fig.4 PO_4^{3-} concentrations in sea water, groundwater, recycled water and rivers

concentrations in the borehole delta water were very low (average, 0.25 mg/l; Fig.4). PO_4^{3-} concentrations for other borehole waters, river and sea waters were also very low. PO_4^{3-} is adsorbed by soil, which in turn was thought to have caused the low concentration of PO_4^{3-} in the borehole delta waters. So, neither NO_3^- nor PO_4^{3-} was a good indicator for recycled water.

In the search for a good indicator for recycled water, next the concentrations of Br^-, F^-, I^-, SO_4^{2-}, and Ca^{2+}, K^+, Li^+ Mg^{2+}, Na^+ ions and total Al, As, Ba, Co, Cr, Cu, Fe, Ga, Hg, Mn, Ni, Pb, Sb, Se, Si, Sr, V, and Zn were measured. The concentrations of F^-, Pb, Sb and V were sufficiently high in the recycled water to be considered as indicators for recycled water.

Fluoride is added to drinking water in Melbourne, and so Melbourne's sewage water may have artificially high F^- levels. So, F^- was thought to be a good indicator of mixing ratio of recycled water. As expected, the recycled water had an extremely high concentration of F^- (average 1.82 mg/l; Fig.5) relative to the sea water (average 0.45 mg/l), the borehole medium (average 0.09 mg/l), borehole upstream (average 0.11 mg/l). F^- concentrations in river waters increased from upstream to downstream (from 0.04 to 0.12 mg/l). Average F^- concentrations for the borehole delta samples was 0.3 mg/l (Fig.5), so some borehole delta water was thought to contain recycled water.

Although F^- itself is stable and is not adsorbed by soil, it may form insoluble complexes with calcium. Such chemical changes by soluble substance during the migration process make them imperfect indicators of mixing. On the other hand, the isotope values for oxygen and hydrogen are stable, making them better indicators of mixing.
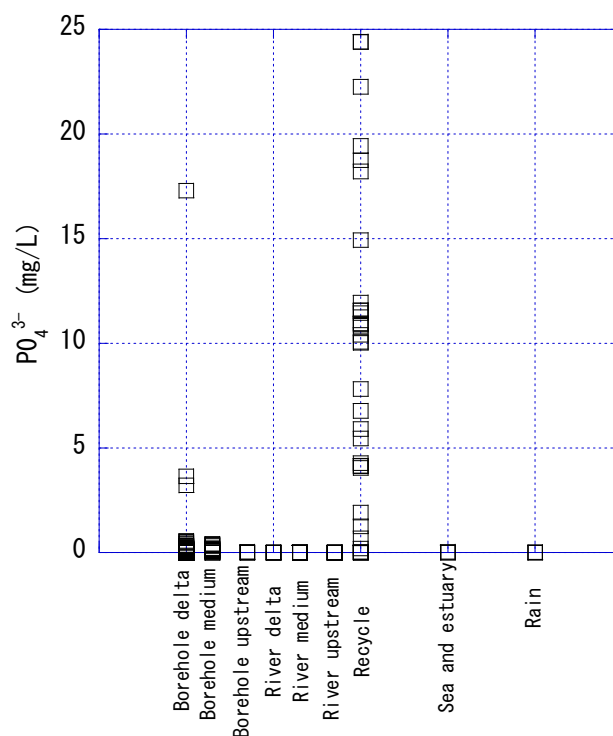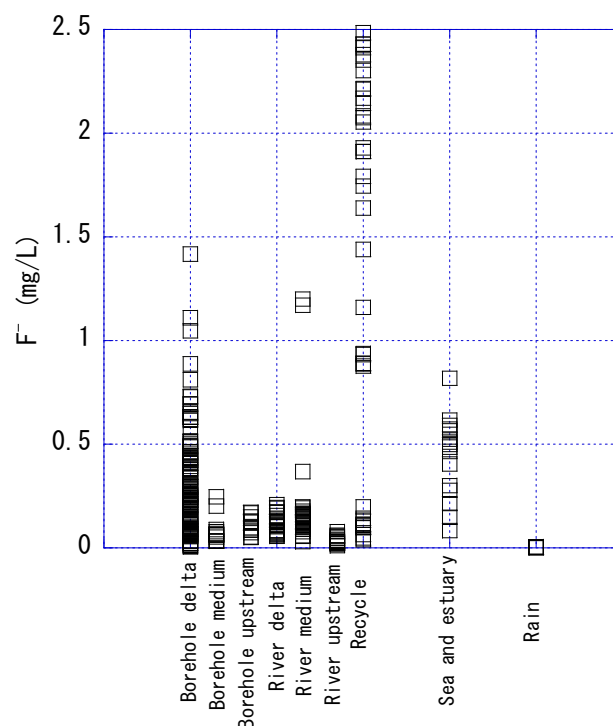

Fig.5 F^- concentrations for sea, groundwater, recycled water and rivers

The oxygen isotopic values ($\delta^{18}O$) for borehole delta waters were -7 to -2 per mill (Fig.6) and these values were similar to those of the recycled water and borehole medium and borehole upstream waters; $\delta^{18}O$ values for sea water (not estuary) were higher than those for the borehole delta waters (Fig.6).
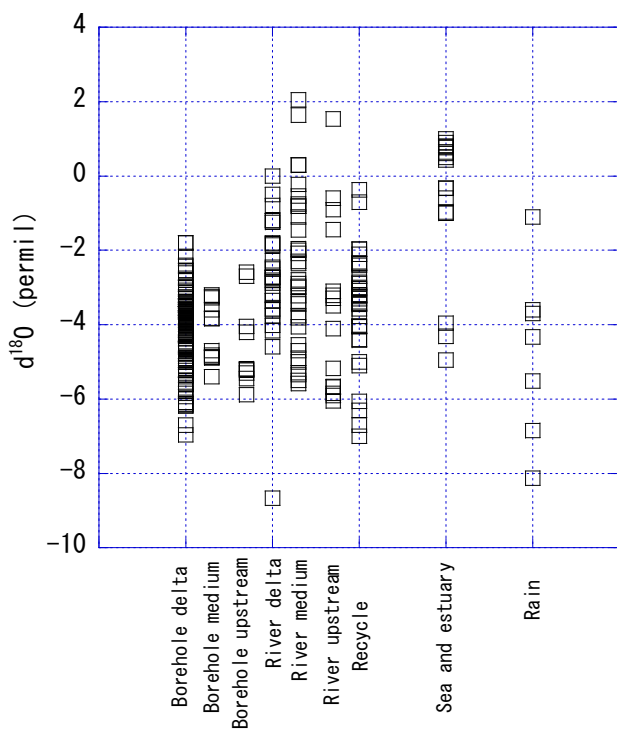
Fig.6 δ^{18}O for sea, groundwater, recycled and river waters

Oxygen isotope values for river delta water were rather variable, but generally higher than those for borehole delta water. For most of the borehole delta sites, the mixing ratio for sea water was thought to be small, whereas the mixing ratio with borehole medium or recycled waters was thought to be large. The oxygen isotopic values for the borehole medium samples was uniform relative to borehole delta samples, and so borehole delta water was thought to be the result of variable mixing with sea water with high isotope values and recycled water with variable isotope values.

3.2 Estimation method of mixing ratio for borehole delta

Groundwater at the delta (borehole delta) was thought to be derived from the sea from, recycled water and river delta water from surface irrigation and upstream groundwater from upper catchment area. Upstream groundwater can be thought of as borehole medium because borehole medium was located at the upstream catchment of borehole delta. Recently, irrigation water has not been sourced from river delta water but recycled water. With respect to their water chemistry, the river delta and borehole medium water were very similar relative to sea and recycled water. The river delta water can be regarded as borehole medium water. Therefore, the three components, sea, recycled and borehole medium waters were used for determining mixing ratios for borehole delta water.

First, because the Cl⁻ concentration of the sea water was extremely high (20,000 mg/l), relative to other waters, Cl⁻ was used for determining the mixing ratio of sea water. The mixing ratio between sea and borehole medium (recharged water; 1,400 mg/l), was calculated using equation (2).

$$Msea1 = (Cl_{sample}\text{-}1400)/(20,000\text{-}1400) \times 100\% \qquad (2)$$

where Cl_{sample} is the Cl⁻ concentration of borehole delta water.

The mixing ratio between the sea and recycled water, 450 mg/l was calculated using equation (3).

$$Msea2 = (Cl_{sample}\text{-}450)/(20,000\text{-}450) \times 100\% \qquad (3)$$

The actual value is between the *Msea1* and the *Msea2*. The difference between the *Msea1* and the *Msea2* was less than 5 %.

Next, because the F⁻ concentration of the recycled water was extremely high (1.82 mg/l), relative to other waters, F⁻ was used for determining the mixing ratio of the recycled water. The mixing ratio between the recycled water and borehole medium (recharged water; 0.09 mg/l), was calculated using equation (4).

$$Mrecycle1 = (F_{sample}\text{-}0.09)/(1.82\text{-}0.09) \times 100\% \qquad (4)$$

where F_{sample} is the F⁻ concentration of borehole delta water. The mixing ratio between recycled water and sea (0.45 mg/l) was calculated using equation (5).

$$Mrecycle2 = (F_{sample}\text{-}0.45)/(1.82\text{-}0.45) \times 100\% \qquad (5)$$

The actual value is between the *Mrecycle1* and the *Mrecycle2*. The difference between the *Mrecycle1* and the *Mrecycle2* was less than 21 %.

3.3 Estimation results of mixing ratio for borehole delta

From Cl⁻ and F⁻, mixing ratio of sea (*Msea1* and *Msea2*) and recycled waters (*Mrecycle1* and *Mrecycle2*) for borehole delta water were estimated, when groundwater at the delta was derived from three components, sea, recycled and borehole medium. Borehole medium mixing ratio was estimated from both the sea mixing ratio and recycle mixing ratio, from which it was shown that borehole medium water was basically the main source of delta groundwater. Borehole medium reaches minimum values when sea mixing ratio between *Msea1* and *Msea2* reaches maximum value and recycle mixing ratio between *Mrecycle1* and *Mrecycle2* reaches maximum value. Fig.7 shows the estimated minimum mixing ratio of borehole medium water and the maximum mixing ratios of recycled and sea waters. Borehole medium reaches maximum values when sea mixing ratio between *Msea1* and *Msea2* reaches a minimum value and recycle mixing ratio between *Mrecycle1* and *Mrecycle2* reaches a minimum value. Fig.8 shows the estimated maximum mixing ratio of borehole medium water and the minimum mixing ratios of recycled and sea waters. Both figures were plotted with distance from the coast. The actual mixing ratio for borehole medium, sea and recycled waters was between both figures. Then, from both figures, the mixing ratio of borehole medium, upstream groundwater mainly was found to vary from 60 to 100 %. From the oxygen isotope data, river delta water was higher than that of borehole delta. As oxygen isotope of borehole medium was similar to those of borehole delta, high mixing ratio of borehole medium was in good agreement with oxygen isotope results. Therefore, the mixing ratio of river delta was thought to be small.
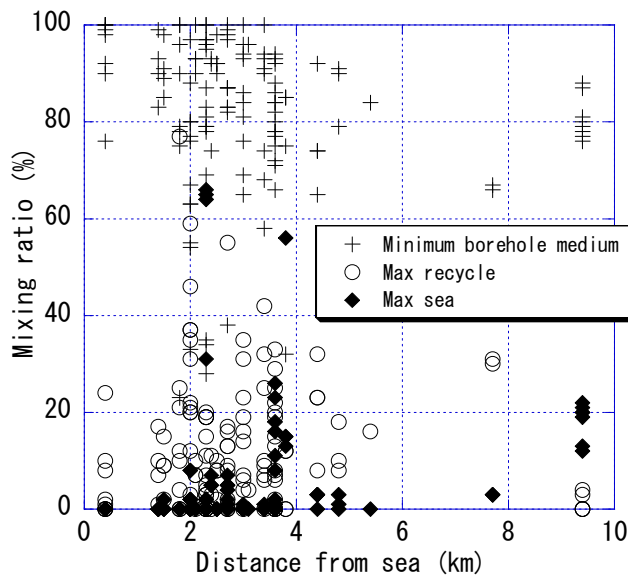
Fig.7 the estimated minimum mixing ratio of borehole medium water and the maximum mixing ratios of recycled and sea waters with distance from the coast
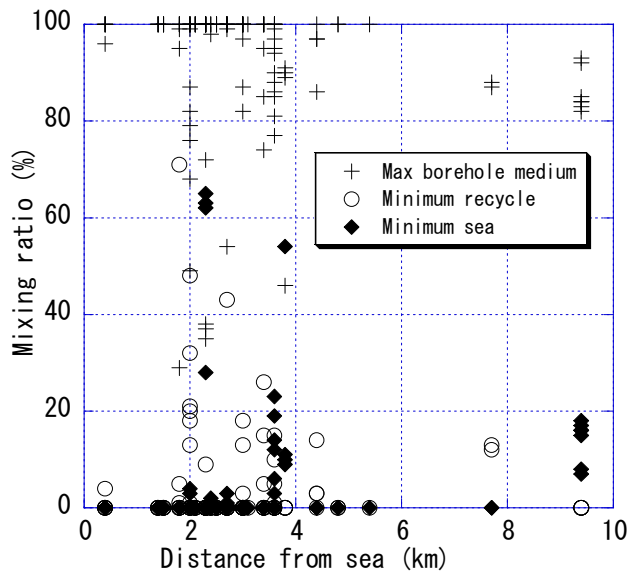

Fig.8 the estimated maximum mixing ratio of borehole medium water and the minimum mixing ratios of recycled and sea waters with distance from the coast
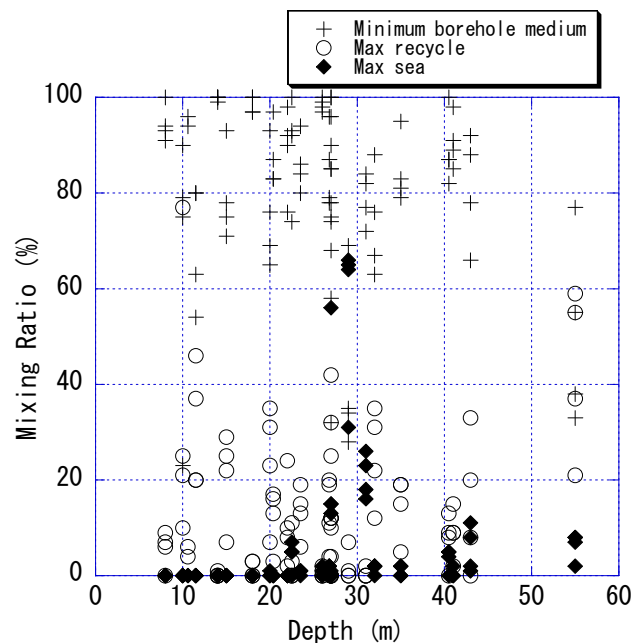

Fig.9 the estimated minimum mixing ratio of borehole medium water and the maximum mixing ratios of recycled and sea waters with depth
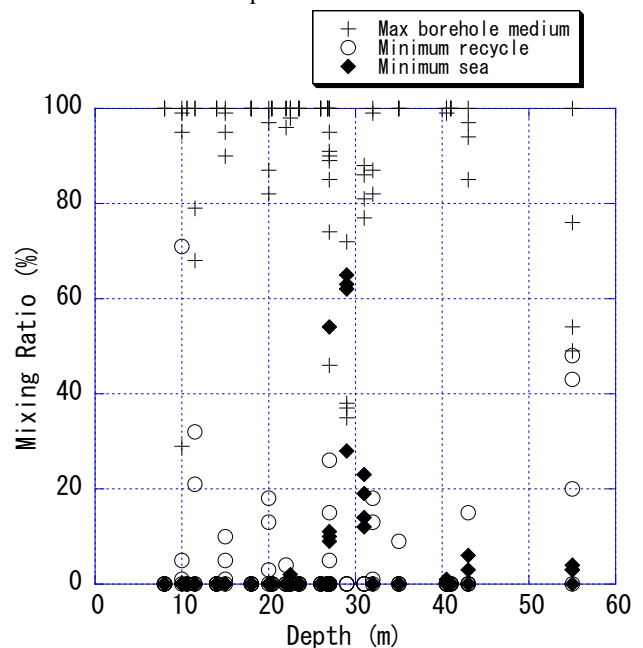

Fig.10 the estimated maximum mixing ratio of borehole medium water and the minimum mixing ratios of recycled and sea waters with depth

Although the sea water mixing ratio for some delta groundwater reached 60 %, the sea water mixing ratio for most delta groundwater was less than 10 %. The $\delta^{18}O$ of the sea water was much higher than those of borehole delta, and so the small mixing ratio was in good agreement with the isotopic data. Overall the sea water mixing ratio was high in the deeper groundwater (e.g. at 30m in depth; Fig. 9 and 10), and this zone is thought to be a salt-water wedge. The sea mixing ratio was not always high near the coast - some groundwater over 9 km from coast showed high sea water mixing ratio (20 %). In this case, the borehole was at the north west of delta facing the Werribee estuary, suggesting there may be salt water intrusion into the groundwater at this point.

The mixing ratio of recycled water varied from 0 to 60 %, but was mainly in the range 10 to 30 %. The 10 to 30 % mixing ratio of recycled water was good in agreement with isotopic data.

The $\delta^{18}O$ of the recycled water was similar to that of borehole delta waters, suggesting that most bore water was contaminated by recycled water. The recycled water mixing ratio was uniform with depth (10 to 30 % at all depths), suggesting that recycled water had infiltrated uniformly down through the permeable Werribee Delta soils, compared to the sea water which intruded laterally at about 30 m depth.

3.4 Contamination for groundwater delta

The F⁻ concentration of many of recycled water samples was over the Australian guideline (trigger) values for short term use of irrigation water (STV, up to 20 yrs); 2.0 mg/l

[5]), and, although the F⁻ concentrations for all borehole delta waters were less than the guideline value (Fig.5), its origin appears to be the recycled water.

Antimony (Sb) concentrations were high in the recycled water (Fig.10). There are currently no Australian guideline values for Sb in irrigation water, but it is a good indicator for groundwater contamination by recycled water.
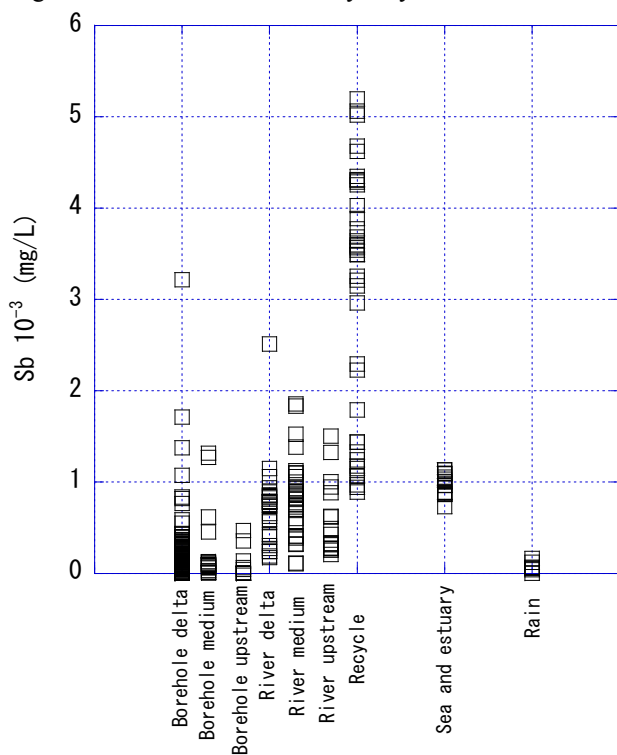

Fig.11 Sb concentrations for sea, groundwater, recycled water and rivers

The STV for arsenic (As) in irrigation water is 2.0 mg/l [5]. This value was not exceeded in any bore water sample (Fig. 11). Similarly, neither of the STVs for Mn and Ni in irrigation water (10 and 2 mg/l, respectively) were exceeded in any bore water sample (Fig.13 and Fig.14).

High concentrations of nitrogen (N) in irrigation water can lead to leaching of N into ground and surface waters, over-stimulation of plant growth (decreasing yields) and the stimulation of algal growth in surface water. The STV range for N in Australian irrigation waters has been set to minimize the risk of contaminating ground and surface water, and is defined by measurements of Total N. because the focus of this study was on specific ionic species in the waters, Total N was not measured, and so no assessment can be made in comparison to irrigation water quality guidelines [5].

4. CONCLUSION

The Werribee Delta is an important irrigated agricultural area for Melbourne, supplying many fresh vegetables to the city. Historically, the Werribee River was used for irrigation water, but because of extended recent droughts its flow decreased, and recycled water from Melbourne's largest waste water treatment plant has had to be used for irrigation. The recycled water contains both domestic sewage and industrial wastewater, and local farmer and water manager concerns have been raised about

groundwater contamination and the sustainability of recycled water use for irrigation. In this study, the water chemistry around the Werribee Delta area was clarified. Using F⁻ and Cl⁻ data, the origins of the groundwater in the delta area was estimated, and the source mixing ratios were calculated. The mixing ratio of the recycled water in the groundwater in the delta varied from 10 to 30 % at all depths in the aquifer, suggesting that the delta groundwater was largely comprised of irrigated recycled water.
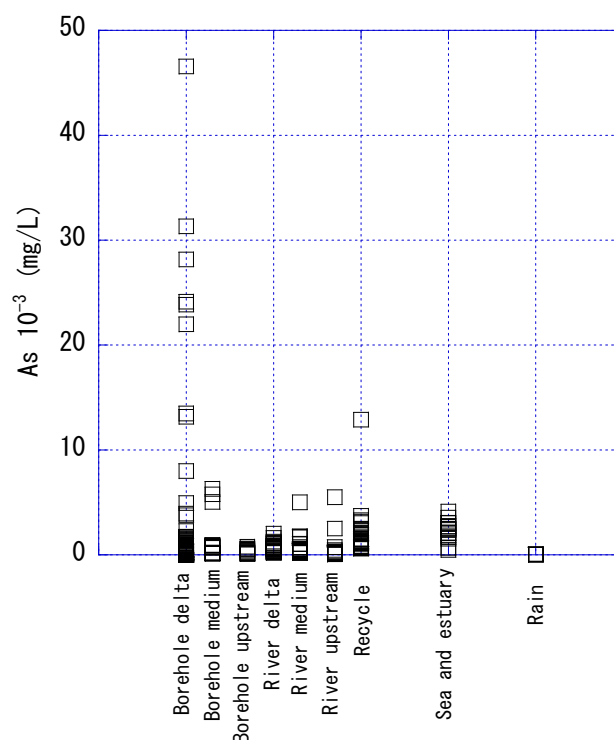

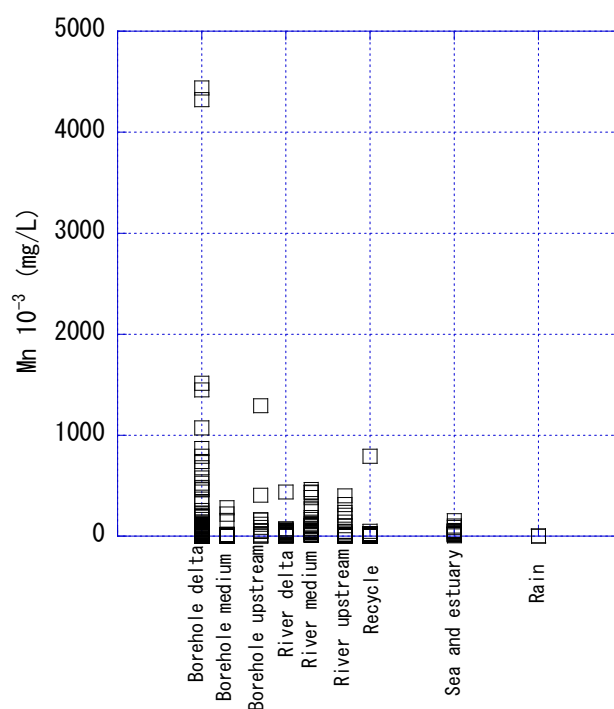Fig.12 As concentrations for sea, groundwater, recycled water and rivers

Fig.13 Mn concentrations for sea, groundwater, recycled water and rivers
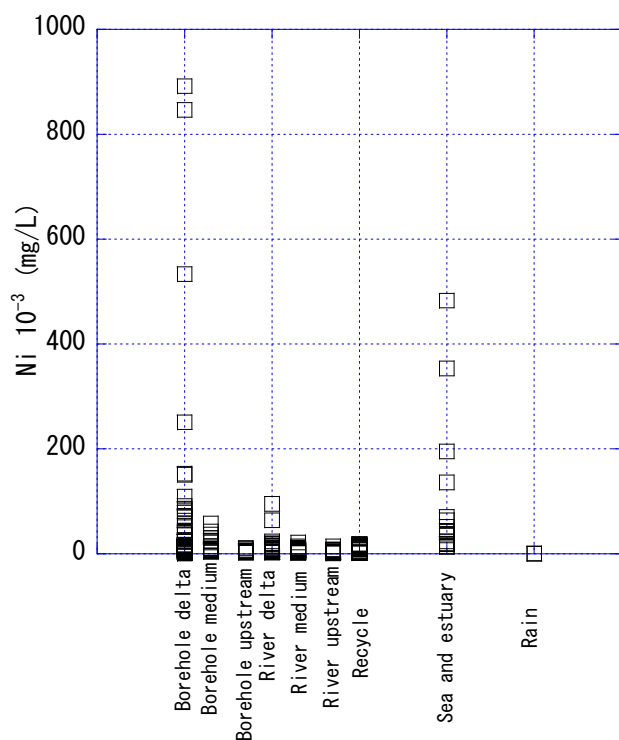
Fig.14 Ni concentrations for sea, groundwater, recycled water and rivers

A high mixing ratio of sea water was found at 30 m in depth in a zone thought to be a salt-water wedge.

Delta groundwater contained 10 to 30 % recycled water and the influence of recycled water on delta groundwater was clarified. PO_4^{3-} and NO_3^- concentrations were high in the recycled water. These were derived from domestic sewage. NO_3^- concentrations for the recycled water were higher than those of recycled water. NO_3^- contamination of the delta groundwater is thought to be caused by both the recycled water and agricultural use of fertilizers because of fertilizer used on the farming delta area. However, PO_4^{3-} concentration in the delta groundwater was not high and PO_4^{3-} was thought to be adsorbed with soil.

Both F and Sb were high in both the delta groundwater and recycled water and indicates the delta water was highly contaminated with F and Sb from the recycled water, the former thought to be of drinking water source and the latter of industrial origin. The STVs for As, Mn and Ni were not exceeded in any bore water samples.

5. REFERENCES

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