CRC FOR CATCHMENT HYDROLOGY
CSIRO LAND AND WATER
MURRAY-DARLING BASIN COMMISSION

ON-FARM AND COMMUNITY-SCALE SALT DISPOSAL BASINS ON THE RIVERINE PLAIN

A RECONNAISSANCE SURVEY OF ELEMENT COMPOSITION AND PESTICIDE LEVELS IN SALINE DISPOSAL BASINS IN THE RIVERINE PLAIN

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Foreword

There are pressures to minimise salt leaving irrigated catchments of the Murray-Darling Basin to limit salinity increases in the River Murray. Part of this strategy is to manage drainage disposal water in the irrigation areas using disposal basins. Unfortunately, there are no existing guidelines for siting, design and management of such disposal basins. The CRC for Catchment Hydrology and CSIRO Land and Water, with support from the Murray-Darling Basin Commission, have embarked on a project with the overall objective of producing such guidelines for the Riverine Plain of the Murray Basin.

This report is one of several being produced in this project to support the guidelines. It deals with water quality in the basin water and sediments. Basin water quality is important in terms of decommissioning, permissible leakage, limits to exposure to the environment and the setting of monitoring guidelines and auditing requirements. The results suggest that while there is nothing of immediate concern, some caution should be exercised with regard to aquaculture, contact with aquatic ecosystems and decommissioning. There is also a need for increasing current monitoring.

Glen Walker
Leader, Salinity Program

Summary

Saline disposal basins have been developed as part of an integrated package to deal with rising watertables associated with irrigated agriculture and have proved to be successful in the disposal of saline groundwaters. Several studies have investigated salt balances and movement of saline leakage from the basins. However, this is the first study to determine whether any potentially toxic levels of inorganic components or pesticides are present in these basins.

The presence of contaminants in these basins may impact on the health of the flora and fauna within the area, may restrict the future use of the basins (for example aquaculture), and upon any decommissioning, may make them unsuitable for return to agriculture or other uses.

This reconnaissance survey involved the analysis of water and sediment samples from five basins in the Murrumbidgee Irrigation Area (MIA) and one in the Shepparton Irrigation Region (SIR).

The results from this study showed that the concentrations of boron, copper, cadmium, lead and manganese were, in some instances, above guideline levels for water and sediments. All of the pesticides included in the study (atrazine, diuron, metalochlor, endosulfan and chlorpyrifos) were detected at levels above guideline levels for the protection of aquatic environments. These pesticides were also found at elevated levels in the sediments. However, the total hardness of these waters is very high (100-300 mg/L) which should greatly reduce the toxicity of heavy metals, and possibly the other contaminants.

These results indicate that the water and sediments in the basins should be regularly monitored and the sites treated as potentially contaminated. Further investigation is required to determine the appropriate guideline levels for these waters and hence appropriate management of these sites.

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1. Introduction

Saline disposal basins have been extensively used in the Riverine Plain to dispose of saline groundwater from horizontal pipe "tile" drainage systems, such as in the Murrumbidgee Irrigation Area (MIA) and groundwater pumped from bores, such as in the Shepparton Irrigation Region (SIR). There have been a number of studies regarding salt concentration in these basins and the leakage of salts from these basins to the groundwater system (Leaney and Christen, 2000). Previous work by Bowmer *et al.* (1998) has shown that there were pesticides in "tile" drainage water in the MIA, and work by Beijert (1999) on copper use in the MIA showed elevated levels of copper in "tile" drainage water and evaporation basins. However, to date little more is known about the presence of these or other possible contaminants in saline disposal basins, which by their nature will evapo-concentrate many dissolved solids. This work undertook to provide a reconnaissance level survey of some of the existing evaporation basins in the MIA and SIR to determine the degree of contamination of the waters and sediments.

The issues associated with water quality in such basins are:

1) The suitability of evaporation basin water for uses such as aquaculture, irrigation or the supply of stock drinking water

2) The effect on flora and fauna that colonise the basins

3) The status of these sites upon any possible decommissioning

1.1 Project Location

Six disposal basins were sampled on the 10 September 1999. The basins were selected on the basis of being small community or on-farm basins, that they had been in constant operation for at least three years, and were in the Riverine plain. Basins suiting these criteria were on-farm basins in the MIA and the Girgarre basin in Victoria.

The MIA basins were all associated with "tile" drainage of vineyards. These are relatively small (<10 ha) basins located on-farm. The basins were selected to give as wide a geographic distribution in the MIA as possible. The Girgarre basin in the Shepparton Irrigation Region (SIR) is a much larger basin (30 ha) accepting water from a groundwater pump in an area of pasture production for dairying. Two bays were sampled at each basin to provide an estimate of differences that may exist between bays in a basin. The selected locations were; in the MIA - Thorne Rd, Barbaro, Nehme, Piva and Debortoli, in the SIR - Girgarre.

2. Methods

Water and sediment samples were collected from each of the locations described above. Standard techniques for sampling were as follows:

- Water samples (1L) were collected according to the method described in Korth and Foster (1998). Samples for the pesticide analysis were collected in pre-cleaned amber bottles, rinsed with sample water 3 times, with the collected sample being adjusted to pH 6.9 using a phosphate buffer prior to storage. Samples for element analysis were collected in acid rinsed bottles and acidified with nitric acid to less than pH 2 prior to storage.
- Sediment samples were collected according to USEPA (USEPA Method 200.2, USEPA 1991) standard methods. The procedure involved the collection of vertical cores using a perspex corer (50 mm diameter). The cores were extruded from the bottom, a horizontal slice of 1 cm in depth was taken from the surface of each of the cores and placed in a pre-cleaned amber bottles for storage.

All samples were processed within 6 hours of collection and stored at -15^{o} C until they were analysed.

2.1 Element Analysis

Acidified water samples and extracted sediment samples were analysed by the Analytical Chemistry Unit, CSIRO Land and Water, Adelaide (USEPA Method 200.8, USEPA 1991) for the elements; Ca, Pb, S, Al, P, Zn, Na, Fe, Co, B, K, Cu, Cd and Mg. Sediment samples (1 gm) were digested using a mixture of nitric and hydrochloric acid at 85^{o} C for 30 minutes. These extracts were then diluted to 100 mL with nanopure water and stored for later analysis (USEPA Method 200.2, USEPA 1991).

2.2 Pesticide Analysis

The samples were analysed for the pesticides atrazine, diuron, metolachlor, endosulfan, and chlorpyrifos.

Sediment and water samples for pesticide analysis were both extracted by liquid-liquid extraction techniques using dichloromethane (DCM). For water samples, 400 mL of the water sample was placed into a separating funnel and extracted with 3 portions of 40 mL of DCM. The three DCM extracts from each sample were combined and placed into an evaporating tube. After reducing the volume to approximately 1mL by evaporation over nitrogen, the extract was placed into a sealed vial and stored at -15^{o} C until analysis by HPLC.

Approximately 1 gm of the sediment sample was placed into a conical flask with DCM and methanol and left agitating overnight. The supernatant was poured off the surface of the sediment, filtered and analysed for pesticides as described above.

All DCM extracts were analysed for herbicides by the Analytical Chemistry Unit, CSIRO Land and Water, Adelaide. The HPLC analysis procedure was performed on a Varian HPLC system with a diode array detector. The operational conditions were injection volume 50 L, mobile phase A: water B: acetonitrile, 70% A for 10 min, 50% A for 15 min, 30% A for 40 min. The column utilised was a C18 Waters (5NVC C18-4 m).

2.3 Quality Assurance / Quality Control

USEPA methods (1991) for sample collection, preservation, and handling of sediments and waters were followed. These methods outline detailed quality control procedures which were followed by the analysing laboratories, including the analysis of a blank sample and Standard Reference Materials (SRM)(National Research Council Canada, 1990) with every batch that was processed.

The analyses of all blanks gave values below the relevant analytical detection limit for all elements and pesticides. This lack of detection indicates that there was no contamination of the samples occurring during the sample collection phase. Recoveries of the elements in the SRMs (PACS-1, BCSS-1) were greater than 90%. All element recoveries have been corrected to reflect the analytical recoveries associated with the digestion/analysis procedures.

3. Results

3.1 Element Composition

3.1.1 Water

Table 1 shows the results of element analysis of the basin waters. The shaded cells indicate those samples which exceeded the Australian and New Zealand Guidelines for Fresh and Marine Water Quality (ANZGFMWQ) published by the ANZECC and ARMCANZ (1999).

Table 1. Composition (mg/L) in basin water samples of elements exceeding guidelines

Location	B	Mn	Na	P	Mg	Cu *	Zn
Thorne Bay1	2.2	<0.05	2600	851	100	<0.02	0.05
Thorne Bay 2	2.6	<0.05	2570	837	98	<0.02	0.05
Barbaro Bay 1	3.6	<0.05	7670	636	1200	<0.02 (0.058)	0.09
Barbaro Bay 2	3.1	<0.05	3780	852	213	<0.02	0.06
Nehme Bay 1	4.2	<0.05	3690	792	254	<0.02 (0.018)	0.06
Nehme Bay2	6.0	<0.05	4640	403	814	<0.02 (0.029)	0.10
Piva Bay 1	9.6	<0.05	7590	1890	272	<0.02	0.06
Piva Bay2	2.9	<0.05	3510	2190	112	<0.02	0.05
Debortoli Bay 1	2.6	<0.05	5060	2810	97	<0.02 (0.017)	0.08
Debortoli Bay 2	3.0	<0.05	4800	2590	98	<0.02	0.05
Girgarree Bay 1	1.9	0.65	52000	473	12160	<0.02	0.09
Girgarree Bay 2	0.4	0.50	5210	501	947	<0.02	0.10
ANZGFMWQ guidelines							
Aquatic ecosystems	0.005	0.05	-	-	-	0.0003	0.002
Use in aquaculture	-	0.1	-	0.1	15	0.005	0.01
Agriculture water use (DCC values)	0.5	0.2	500	-	-	0.2	2
Livestock drinking water	5	-	2000-5000	-	-	0.5-5	20

Cu* Copper values in brackets are those reported by Beijert, M. (1999) at the same sites.

DCC values are the Desirable Contaminant Concentration which is the maximum concentration that can be tolerated in long-term use irrigation water.

These results show that the guideline levels for aquatic ecosystems in water were exceeded for all basins with respect to boron and zinc, and in the Girgarre basin, for manganese. The latter two were also above the values set for aquaculture, together with phosphorus and magnesium. The sodium level in the water samples in all basins was significantly greater than that which is tolerable to plants (ranging from 5 to 100 times greater than acceptable levels). The guideline levels of boron in all basins and manganese in the Girgarre basin were also exceeded with respect to agricultural usage.

Copper values were above the guideline values for ecosystem protection in some basins from data reported by Beijert (1999). However, in this study the detection level of copper was 0.02 mg/L and no values were found to be above this level.

These guidelines are generally for freshwater environments. Sampling by Beijert (1999) found that in three basins of the MIA, water hardness ranged from 148-288 mg/L ($CaCO_3$). This will greatly reduce the toxicity of heavy metals in this type of water as stated in the ANZGFMWQ, where water is considered hard if greater than 50 mg/L.

Table 2 shows the composition of elements found in the basin water samples which did not exceed guideline values or for which there are no guidelines given.

Table 2. Composition (mg/L) in basin water samples of elements below guidelines or for which there are no guidelines found

Location	Ca	K	S	Fe	Al
Thorne Bay1	9.2	1670	279	< 0.1	< 0.1
Thorne Bay 2	9.1	1630	278	< 0.1	< 0.1
Barbaro Bay 1	155	2010	1960	< 0.1	< 0.1
Barbaro Bay 2	32.8	2140	881	< 0.1	< 0.1
Nehme Bay 1	20.1	1780	895	< 0.1	< 0.1
Nehme Bay2	72.6	930	1430	< 0.1	< 0.1
Piva Bay 1	22.9	3860	2130	< 0.1	< 0.1
Piva Bay2	2.8	4020	348	< 0.1	< 0.1
Debortoli Bay 1	7.8	5040	392	< 0.1	< 0.1
Debortoli Bay 2	5.1	4690	413	< 0.1	< 0.1
Girgarree Bay 1	525	2040	3700	< 0.1	< 0.1
Girgarree Bay 2	75.6	1220	512	< 0.1	< 0.1
ANZGFMWQ guidelines					
Aquatic ecosystems	-	-	-	-	0.001
Use in aquaculture	-	-	-	0.01	0.03
Agriculture water use (DCC values)	-	-	-	0.2	5
Livestock drinking water	-	-	-	-	5

3.1.2 Sediment

The analysis of the element composition of the sediments is shown in Table 3, together with the ANZGFMWQ guideline values for sediments. Table 4 shows the results of the sediment analyses of elements for which there were no guideline values. Concentrations of cadmium were above the 'low' sediment guideline in a majority of samples. The only other elevated results were two lead samples. No samples were at the dangerous 'high' level in any basin.

Table 3. Composition (mg/kg) in basin sediment samples of elements for which guidelines were found

Location	Cd	Cu	Pb	Zn
Thorne B1	0.9	6	19	24
Thorne B2	3.1	6	30	34
Barbaro B1	1.4	14	20	45
Barbaro B4	1.5	18	8	47
Nehme B1	1.4	14	16	34
Nehme B2	2.4	21	61	53
Piva B1	1.5	15	18	10
Piva B2	1.7	14	18	33
Debortoli B1	3.6	21	79	51
Debortoli B2	1.0	10	14	21
Girgarree Bay 1	2.0	2	28	11
ANZGFMWQ guidelines (sediments)				
Low	1.5	65	50	200
High	10	270	220	410

The cadmium and lead levels being at the 'low' level require assessment of availability and toxicity to determine further action under the ANZGFMWQ sediment guidelines. Thus these basins may be assessed as contaminated sites.

Table 4. Composition (mg/kg) in basin sediment samples of elements for which no guidelines were found

Location	Al	B	Ca	Co	Fe	Mn
Thorne Bay1	8650	30	38100	3.2	10400	163
Thorne Bay 2	9110	67	183000	5.9	8930	166
Barbaro Bay 1	1680	111	24800	8.4	21000	907
Barbaro Bay 2	26300	92	40900	8.2	28400	360
Nehme Bay 1	11300	96	80000	6.5	15800	251
Nehme Bay2	17900	231	41100	10.6	24300	695
Piva Bay 1	19200	70	32100	8.3	21800	330
Piva Bay2	24800	95	27600	8.6	23400	273
Debortoli Bay 1	20500	161	94900	9.7	26600	295
Debortoli Bay 2	10100	81	5070	5.2	14100	163
Girgarree Bay 1	68	15	46	5.0	76	5

Table 4 continued

Location	Mg	Mo	Na	P	K	S
Thorne Bay1	4600	2	1560	119	2790	590
Thorne Bay 2	7270	8	8610	219	2890	3690
Barbaro Bay 1	11400	3	8270	151	5660	6380
Barbaro Bay 2	10900	4	3690	182	7890	1410
Nehme Bay 1	6950	3	5060	317	4020	7010
Nehme Bay2	16700	6	12800	389	6920	9220
Piva Bay 1	7600	4	3980	102	6830	3380
Piva Bay2	78800	42	26200	1890	5970	7810
Debortoli Bay 1	8970	9	7950	991	6150	2560
Debortoli Bay 2	5830	2	1920	199	3390	671
Girgarree Bay 1	19	5	58	13	19	75

3.2 Pesticide Composition

3.2.1 Water

Most basins were found to have one or more pesticides present of those included in this study, as shown in Table 5.

Table 5. Pesticide concentration (g/L) in basin water samples

Location	Atrazine	Diuron	Metalochlor	Endosulfan	Chlorpyrifos
Thorne B1	ND	ND	ND	ND	ND
Thorne B2	0.65	ND	ND	ND	ND
Barbaro B1	ND	ND	0.28	ND	ND
Barbaro B4	ND	ND	ND	ND	0.38
Nehme B1	ND	0.25	ND	5.93	ND
Nehme B2	ND	ND	ND	2.08	ND
Piva B1	ND	ND	ND	ND	ND
Piva B2	ND	ND	ND	ND	ND
Debortoli B1	ND	ND	ND	0.95	ND
Debortoli B2	ND	ND	ND	ND	ND
Girgarree Bay 1	2.83	ND	ND	ND	ND
Girgarree Bay 2	ND	ND	ND	ND	0.58
ANZGFMWQ guidelines					
1) Aquatic ecosystems	0.5	*	*	0.001	0.001
2) Aquaculture #	0.34	1.5	-	0.003	0.001
3) Agriculture water use (DCC values)	++	+++	-	-	
Murrumbidgee Irrigation drainage licence (NSW EPA, Griffith)					
1) Notification level	2	8	8	0.05	0.001
2) Action level	10	40	40	0.1	0.005

ND Indicates that the concentration of the pesticide was below the detection limit of 0.25 g/L

* Guidelines were not specific, but compound considered to be toxic

interim values only

++ moderate and +++ high hazard to crops

The pesticide when detected was usually present at a concentration significantly greater than that for water use in aquaculture or for protection of ecosystems. The values were all well below the raw drinking water guideline.

3.2.2 Sediments

Pesticides were also frequently detected in the sediment samples, as shown in Table 6. Atrazine was detected at elevated concentrations in all basins. Chlorpyrifos and metalochlor were also detected in more than half the basins sampled.

Table 6. Pesticide concentration (mg/kg) in the sediments of evaporation basin

Location	Atrazine	Diuron	Metalochlor	Endosulfan	Chlorpyrifos
Thorne B1	18.25	ND	0.60	ND	0.05
Thorne B2	50.70	ND	ND	ND	0.18
Barbaro B1	17.24	ND	0.26	ND	0.05
Barbaro B4	16.44	ND	ND	0.50	ND
Nehme B1	16.19	ND	ND	ND	0.05
Nehme B2	22.40	ND	ND	1.16	ND
Piva B1	15.16	ND	ND	ND	ND
Piva B2	21.60	ND	0.08	ND	ND
Debortoli B1	12.48	0.07	0.22	0.82	ND
Debortoli B2	13.55	0.48	0.12	ND	0.08

ND Indicates that the concentration of the pesticide was below the detection limit of 0.05 mg/kg

At present there are no ANZGFMWQ guidelines for these pesticides in sediments. Hence, the toxicity of these samples is unclear; values quoted for dieldrin (a similar compound to endosulfan) are 0.02 g/kg for the 'low' value and 8 g/kg for the 'high' level. Taking these values as being indicative of the toxicity of endosulfan, it would appear that the levels shown in the above table for endosulfan are above both of these values. In order to predict the effect on aquatic ecosystem health from these pesticides, some site specific toxicity data is required.

3.3 Differences Between Basins and Bays

The results for all elements and pesticides varied greatly between basins. This variation reflects site conditions, soil type and groundwater composition, as well as farm management such as pesticide application practices. The samples and understanding of the basin site conditions and farm management are not sufficient to draw any conclusions as to the factors behind the wide variation in results.

The differences between bays within a basin were marked, e.g. pesticides being detected in only one bay of a disposal basin. For some elements such as sodium and magnesium there were also large differences between bays in the same basin. This may be due to evapo-concentration as water passes from one bay to the next.

These results indicate the importance of sampling at more than one bay in a disposal basin to gain a more complete picture of the water composition.

4. Discussion

4.1 Contaminants in Basin Waters

The use of these waters for aquaculture would appear to be restricted due to elevated levels of some elements and pesticides. Where no specific guideline value is available for aquaculture, it would be possible to use the guideline level for protection of aquatic ecosystems. Many of the guideline levels for protection of aquatic ecosystems were exceeded in this sampling. However, the toxicity of the heavy metals and possibly other inorganic contaminants can be expected to be reduced by the water hardness. Thus the actual toxicity to flora and fauna using these basins is unknown.

Apart from the obvious problem of high salinity, the only other apparent restrictions in using this water for irrigation would be associated with the presence of boron and manganese. In these samples the water would need to be diluted with 'fresh' irrigation water to at least 1 part in 10 to reduce the levels of boron and manganese below the guideline level.

4.2 Contaminants in Sediments

The levels of the inorganic elements in the samples of sediment were above the 'low' level for cadmium and lead and hence, further testing is required to determine bioavailability of these contaminants.

The levels of pesticides in the sediment were relatively high and may be of concern, however no guidelines for these pesticides are available for sediments as yet.

From these results it would appear that these types of evaporation basins should be tested for contaminants upon decommissioning as some contaminants may have accumulated in the sediment to a level that would cause the site to be classified as contaminated. In this study, cadmium in the sediment was frequently above the NSW EPA (1999) guideline for agricultural land.

5. Conclusions

This reconnaissance survey of a number of saline disposal basins indicates that there may be some areas of concern with regard to contaminants in the basin water and sediments. The main concerns are related to some inorganic contaminants, especially cadmium and pesticides, especially endosulfan, chlorpyrifos and metalochlor. These contaminants were found at elevated levels in all the basins, and hence not restricted to any particular area or land use.

The use of these types of basins for aquaculture with water of this quality would be restricted.

The water quality in these basins exceeded guidelines for protecting aquatic ecosystems. However, water hardness in these types of basins is extremely high which can be expected to reduce the toxicity of heavy metals and possibly other contaminants.

Elevated levels of some heavy metals and pesticides in basin sediment indicate that there should be an investigation of these sites upon any decommissioning to assess whether the sites are contaminated. The 'Duty to Report' in NSW as set out in the NSW EPA guidelines should be considered (NSW EPA 1999).

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