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Mangrove soils as sinks for wastewater-borne pollutants

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Key words: mangrove, soil/sediment, wastewater, sink, nutrients, heavy metal

Abstract

Soil column leaching experiments were conducted to assess the retention of nutrients and heavy metals in two types of mangrove soils receiving strong wastewater throughout a period of 5 months. NH_4^+-N was the dominant form of nitrogen, nitrite and nitrate were in relatively low concentrations in all leachate collected. The concentrations of NH_4^+-N in leachate collected from columns packed with Sai Keng of Hong Kong mangrove soil were higher than those packed with soils collected from Shenzhen of China. The leachate NH_4^+-N contents of Shenzhen columns were significantly lower than that of the synthetic wastewater even at the end of the experimental period, indicating Shenzhen soils had very high capacity to bind nitrogen, and the amount of ammonium added from wastewater did not exceed the binding capacity of mangrove soil. The data also suggest that soils collected from Shenzhen mangrove swamp had higher capacity in retaining wastewater nitrogen than the Sai Keng soils. In contrast, leachate from Sai Keng columns had significantly lower ortho-P contents than those from Shenzhen columns. Actually, the leachate P concentrations of the Sai Keng columns treated with wastewater were similar to those receiving seawater (< 0.1 mg l^{-1}). This finding implies Sai Keng soils were very effective in retaining wastewater P. Throughout the experiment, most heavy metals, including Cu, Zn, Cd, Ni and Cr were not detected in all leachate samples by flame atomic absorption spectrophotometry, indicating that both types of mangrove soils were capable of trapping wastewater-borne heavy metals. The study demonstrates that mangrove soils were good traps to immobilize wastewater-borne phosphorus and heavy metals but they were less efficient in retaining nitrogen from wastewater.

Introduction

Wetland (both natural and constructed) have been used as biological systems for effluent purification and are attractive to the industry as they provide an alternative low-cost, low-maintenance and simple method for domestic and industrial sewage treatment (Clough *et al.*, 1983; Harbison, 1986; Conley *et al.*, 1991). The entire wetland soil-plant-water system, which provides both aerobic and anaerobic conditions, is important in the reduction of nutrients, heavy metals and even organic pollutants from wastewater (Ambus & Lowrance, 1991; Dunbabin & Bowmer, 1992). The relative significance of plants and soils in the removal of pollutants in wetland is a subject of debate. Rogers and co-workers (1991) found that in a constructed wetland, plant uptake accounted for 85% of the total nitrogen reduction and thus the importance of plant component in the whole system was emphasized. However, due to senescence, vegetative uptake could only be considered as a temporary storage mechanism and required removal through harvesting. Therefore the soil and its indigenous microbial populations would ultimately immobilize the added nutrients (Burgoon *et al.*, 1990). Johnston (1991) stated that the total amounts of nutrients stored in the soil fraction were far higher than other storage compartments of a wetland system, and once the nutrients entered the soil component, they were retained there for an extended period. Soils of coastal marshes can also be acted as sinks for heavy metals such as Zn, Pb and Cd (Banus *et al.*, 1975).

The mechanisms involved in the immobilization of pollutants in the soil component of a wetland system include adsorption on ion exchange sites, binding

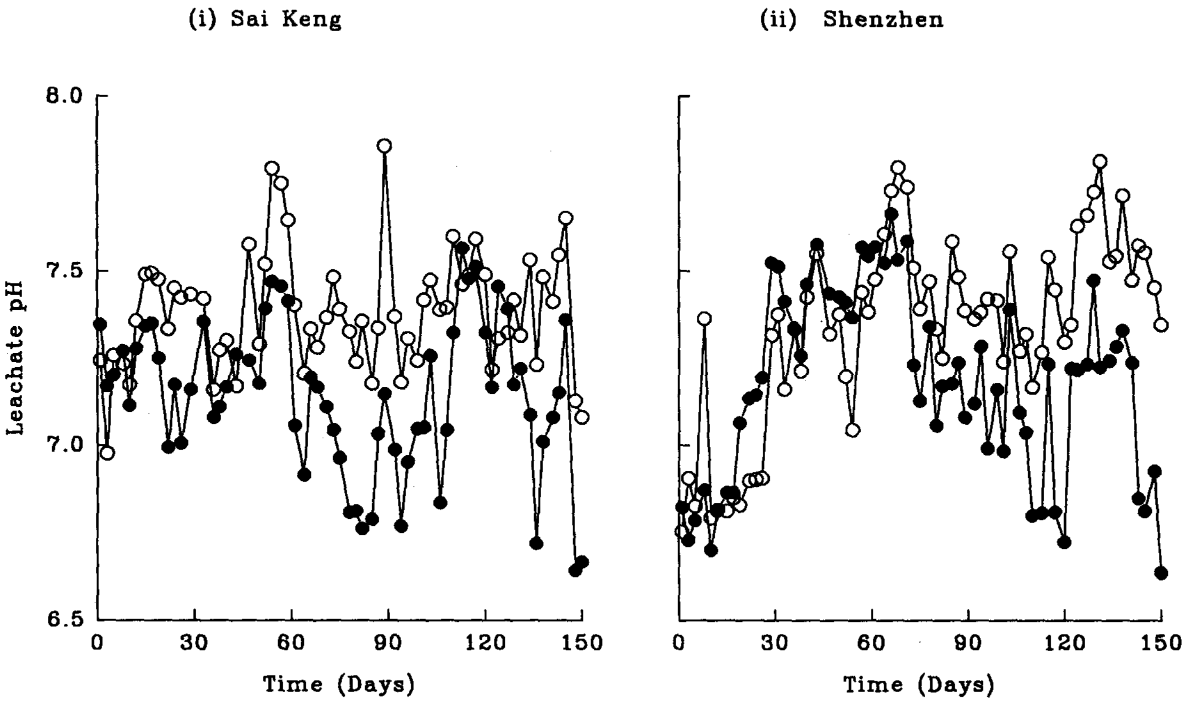

Fig. 1. pH values (mean of 3 replicates) of leachate collected from the control and treated columns of Sai Keng and Shenzhen soils. (o: seawater control; •: wastewater treatment; ANOVA results showed that there was no significant difference between control and treated columns, and also no difference between the two soil types)

to organic matter, incorporation into lattice structures, and precipitation into insoluble compounds (Chan *et al.*, 1982; Dunbabin & Bowmer, 1992). Microbial-mediated reactions including oxidation and reduction, nitrification and denitrification also determined the fate of pollutants in wetland system (Reed *et al.*, 1988; Dunbabin & Bowmer, 1992). All these processes are affected by the biological, chemical and physical properties of wetland soils, in particular pH values, texture, porosity, cation exchange capacity, redox potential, salinity, contents of organic matter, oxides and hydroxides of iron, manganese and aluminium, carbonates, phosphates and sulphide, microbial population sizes and activities (DeBustamante, 1990). Different wetland systems of varied soil characteristics will have different capacity to trap nutrients and heavy metals from wastewater. Mangrove ecosystems, one of the major types of natural wetland in tropical regions, appear to possess high capacity to retain wastewater-borne pollutants. This might be attributed to their anaerobic and reduced conditions, periodic flooding by incoming and outgoing tides, and high clay and organic matter content. Over the past few decades, mangrove swamps have often been deliberately used as convenient dumping sites for waste and sewage in many developing countries (Clough *et al.*, 1983; Dwivedi & Padmakumar, 1983). Although it seems possible to employ mangrove ecosystems as wastewater treatment facilities, the significance of mangrove soil in retaining nutrients and heavy metals from wastewater is poorly understood, especially in sub-tropical mangrove swamps. The present soil column study is therefore aimed (1) to examine the ability of mangrove soils in purifying nutrients and heavy metals from wastewater of high strength; and (2) to compare the effectiveness of two mangrove soils in retaining these wastewater-borne pollutants.

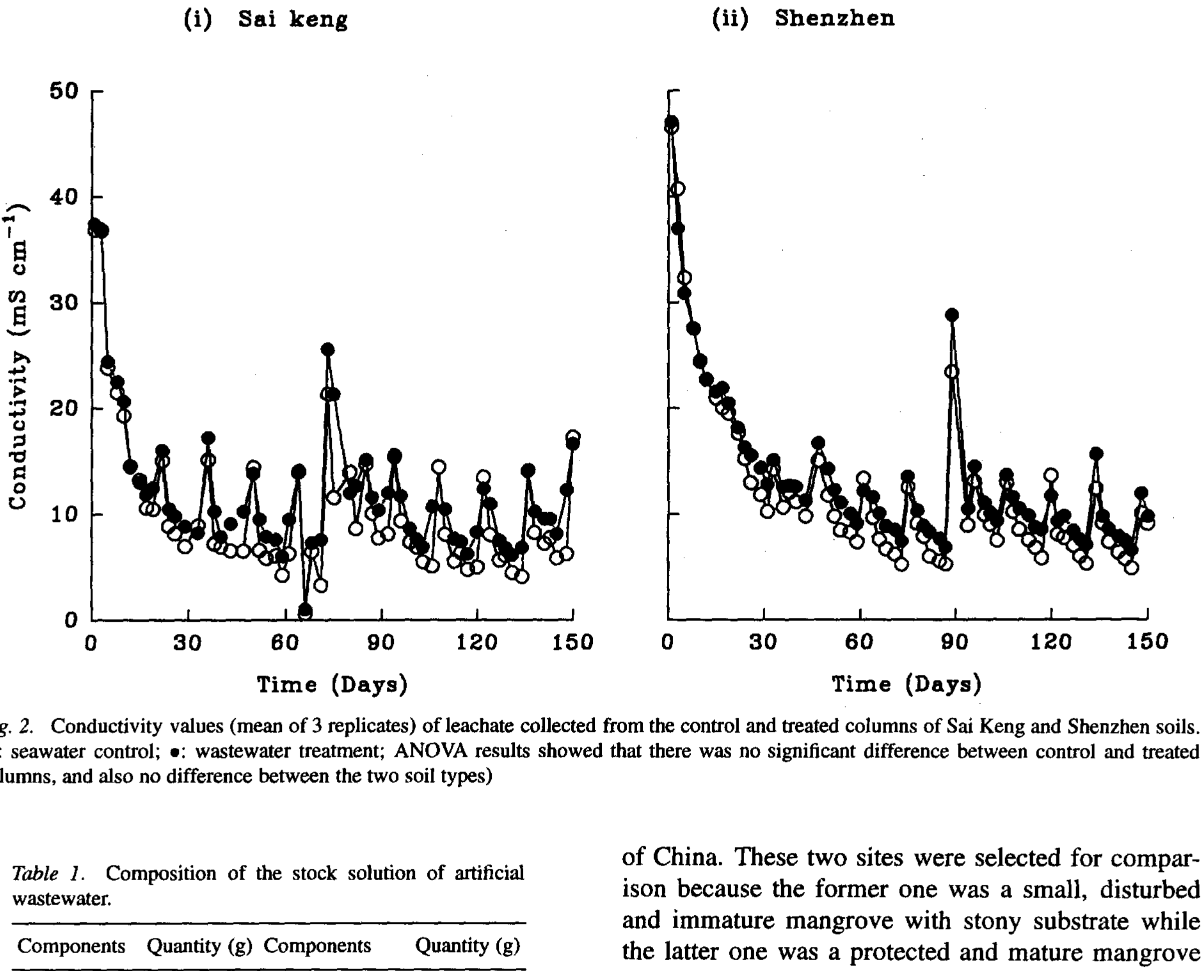

Fig. 2. Conductivity values (mean of 3 replicates) of leachate collected from the control and treated columns of Sai Keng and Shenzhen soils. (o: seawater control; •: wastewater treatment; ANOVA results showed that there was no significant difference between control and treated columns, and also no difference between the two soil types)

Table 1. Composition of the stock solution of artificial wastewater.

Components	Quantity (g)	Components	Quantity (g)
KH_2PO_4	4.39	$CuSO_4 \cdot 5H_2O$	0.39
KCl	7.13	$MnSO_4 \cdot 4H_2O$	2.00
$NaNO_3$	0.61	$ZnSO_4 \cdot 7H_2O$	2.20
NH_4Cl	15.28	$3CdSO_4 \cdot 8H_2O$	0.02
Bactopeptone	5.88	Deionized water	100 ml
Glucose	20.01		

Materials and methods

Mangrove soils

Bulk samples of surface soil (0–10 cm) were collected from two mangrove swamps, one in Sai Keng, Hong Kong, and the other in Futian Nature Reserve, Shenzhen Special Economic Zone, the People's Republic of China. These two sites were selected for comparison because the former one was a small, disturbed and immature mangrove with stony substrate while the latter one was a protected and mature mangrove with muddy soil. The soil was air-dried, ground to pass a 2-mm sieve, thoroughly mixed and stored at room temperature. Subsamples of the soils were analyzed for pH and conductivity (1:10 water extract), texture (wet sieving), organic matter (loss on ignition), ammonium, nitrite and nitrate (1:4 2M KCl extraction followed by Kjeldahl steam distillation), Kjeldahl nitrogen (micro-Kjeldahl digestion and distillation) and ortho-phosphorus (Olsen *et al.*, 1954). Total P content was determined by analyzing the Kjeldahl digest using ascorbic acid-molybdenum blue colorimeter method (Murphy & Riley, 1962). Total K and heavy metals (Cu, Zn, Mn, Cd and Ni) concentrations were measured by dissolving the ash (after ignition at 550 °C for 8 hours) in 6M HCl overnight, followed by flame atomic absorption spectrophotometry. The available heavy metal content (1:10 1M ammonium acetate pH 4 extraction) was also determined by flame atomic absorption spectrophotometry.

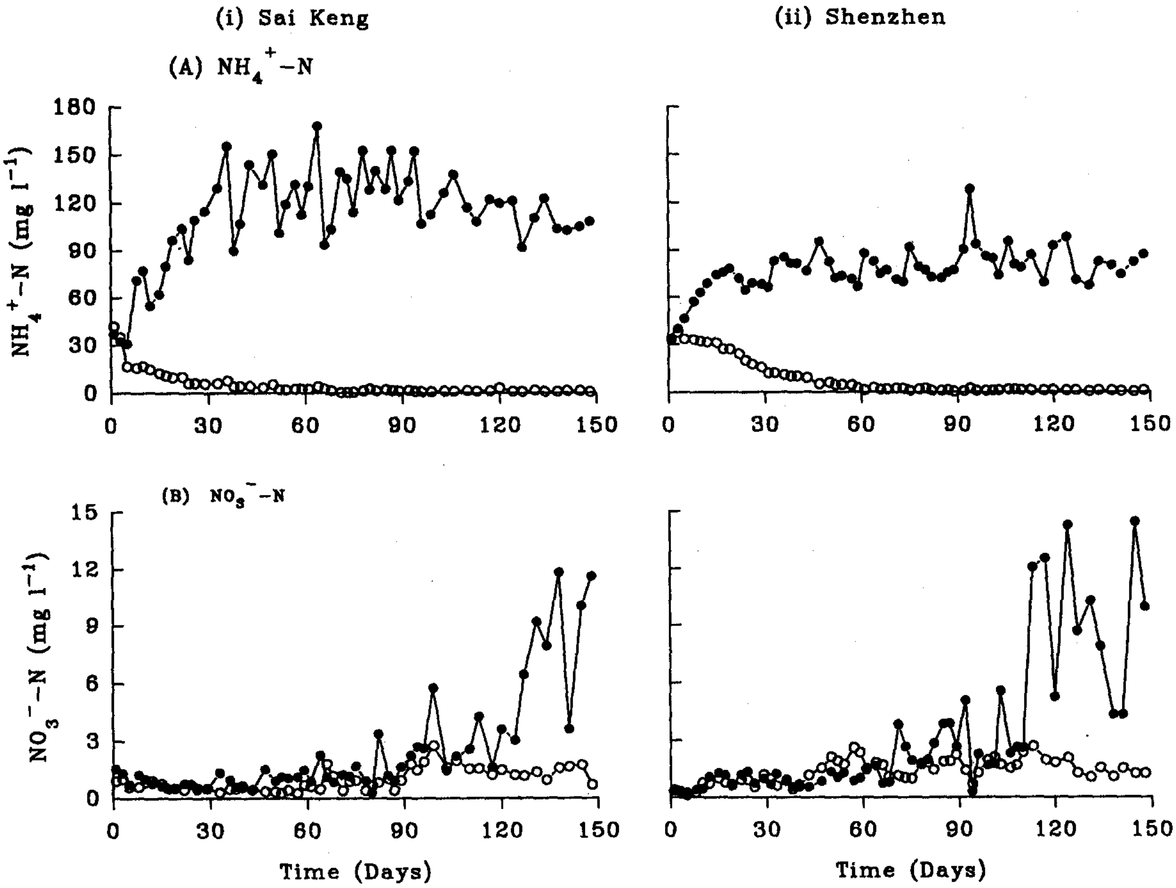

Fig. 3. NH_4^+- and NO_3^--N concentrations (mean of 3 replicates) of leachate collected from the control and treated columns of Sai Keng and Shenzhen soils. (o: seawater control; •: wastewater treatment; For NH_4^+-N: ANOVA results showed that the treated columns had significantly higher ammonium level than the control columns, and significant difference was found between the two soil types; For NO_3^--N: no significant difference was found between the two soil types, and the treated columns had significantly higher nitrate level than the control from day 90 onwards)

Set-up of soil column leaching experiment

Polyvinyl chloride columns (70 cm in length by 10 cm in diameter) were packed uniformly with air-dried soil to a 20- cm depth with a bulk density of 1.02 g cm^{-3}. The columns were initially saturated with artificial seawater for few days. The artificial seawater was obtained by dissolving commercially available salts in deionized water. A complete randomized block design of triplicates was used, and a total of 12 columns were set up for two types of mangrove soil from two sites, namely Sai Keng and Shenzhen, each leached with either artificial seawater (control) or wastewater (treated). The artificial wastewater was prepared by diluting the stock solution (Table 1) 250 times with deionized water and its pH was adjusted to 6.5 ± 0.5. The wastewater consisted of 160 mg l^{-1} NH_4^+-N, 4 mg l^{-1} NO_3^--N, 48 mg l^{-1} organic N, 40 mg l^{-1} PO_4^{3-}-P, 320 mg l^{-1} TOC (total organic carbon), 1094 mg l^{-1} COD (chemical oxygen demand), 200 mg l^{-1} K, 4 mg l^{-1} Cu, 20 mg l^{-1} Zn, 20 mg l^{-1} Mn and 0.4 mg l^{-1} Cd. Its strength was four times of that found in local municipal sewage (Wu, personal communication). A quantity of 200 ml freshly prepared wastewater was applied to each treated column thrice a week. The water was allowed to percolate through and discharge from the

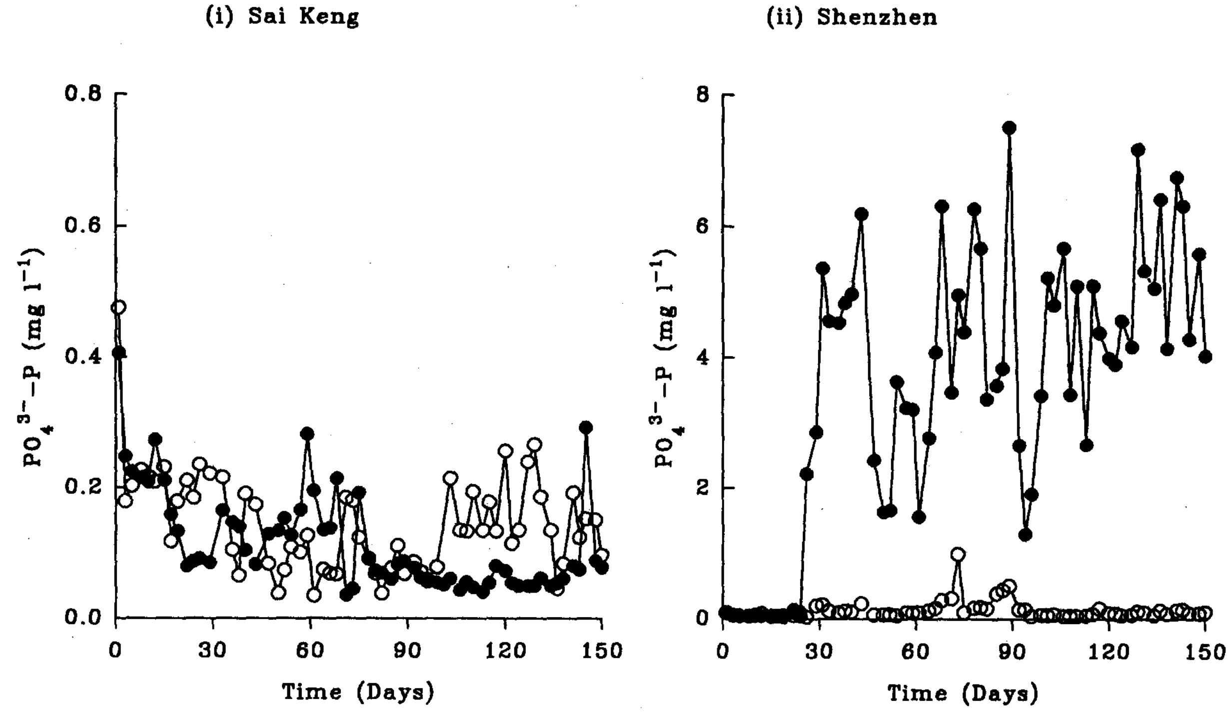

Fig. 4. PO_4^{3-}-P concentrations (mean of 3 replicates) of leachate collected from the control and treated columns of Sai Keng and Shenzhen soils. (o: seawater control; •: wastewater treatment; ANOVA results showed that there was no significant difference between the control and treated columns in Sai Keng soils which had significantly lower phosphorus level than Shenzhen (note the difference in PO_4^{3-}-P scale between the two graphs), the treated columns of Shenzhen had significantly higher phosphorus level than the control)

bottom of the column by gravitational force. For the control columns, artificial seawater, prepared by dissolving the commercially available salts in deionized water with pH adjusted to 6.5 ± 0.5, instead of wastewater was added. After the water had totally drained from the column, the soil was left to dry for 8–10 hours. The column was then re-filled with seawater and left to soak overnight. The seawater was then allowed to drain through the columns, collected and reused. This operation scheme simulated the natural periodic wetting (flooded by incoming tide) and drying (exposed due to outgoing tide) of a mangrove ecosystem. The seawater imitated the flooding tidal water was changed at every two weeks intervals. The whole experiment lasted for 150 days.

Analysis of leachate samples

The leachate collected from each column were analyzed for pH, electrical conductivity, total organic carbon (TOC), NH_4^+-, NO_2^- and NO_3^--N, PO_4^{3-}-P, K, Cu, Zn, Mn, Ni, Cr and Cd, according to the standard methods for water and wastewater analyses (APHA *et al.*, 1989). The mean and standard deviations of the triplicates were calculated. All data on the leachate properties were analyzed by 3-way analysis of variance (ANOVA): the difference between the treated and the control columns, between soil types, and among sampling time were determined. The percentage of the wastewater-borne pollutants retained in mangrove soil was computed based on the difference between quantities added to the column and the quantities of solute in the leachate.

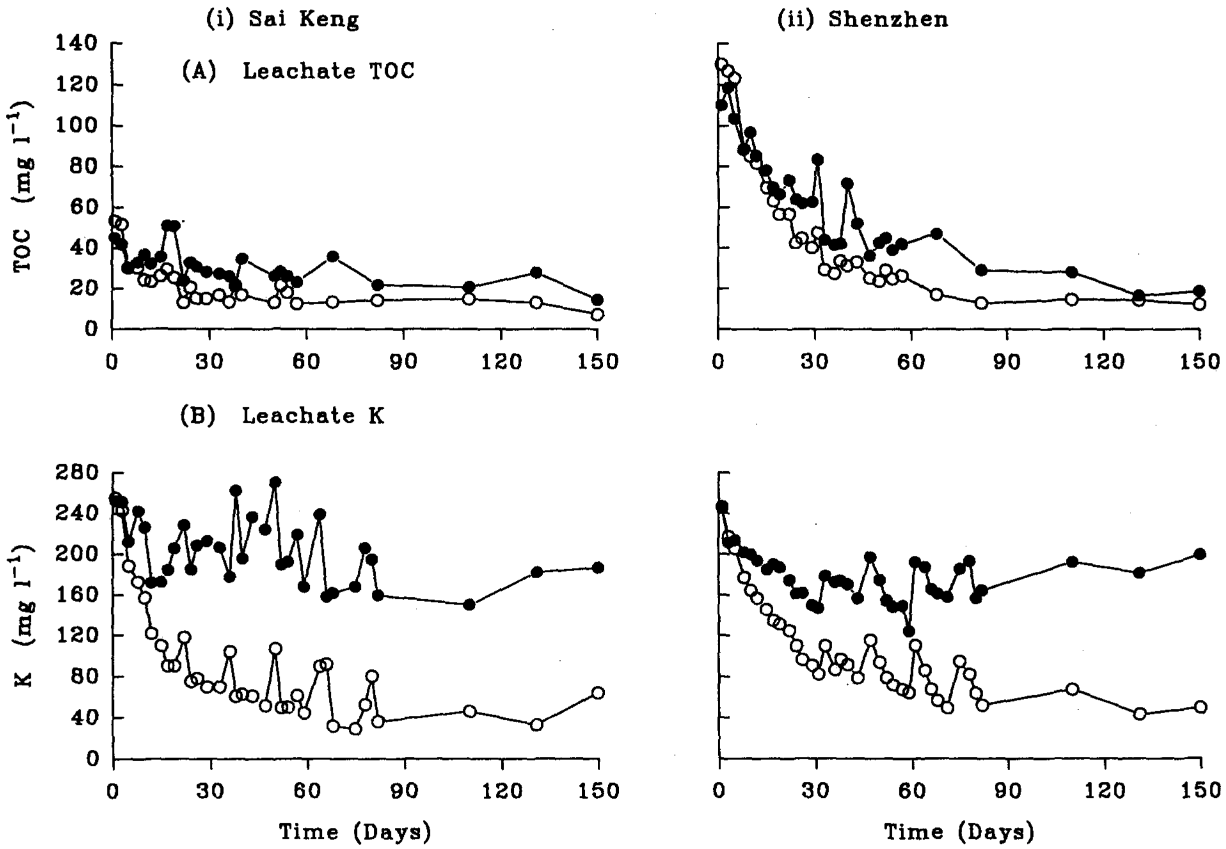

Fig. 5. TOC and K concentrations (mean of 3 replicates) of leachate collected from the control and treated columns of Sai Keng and Shenzhen soils. (o: seawater control; •: wastewater treatment; For TOC: ANOVA results showed that there was no difference between the treated and control columns but significant difference was found between the two soil types; For K concentration: no significant difference was found between the two soil types but the treated columns had significantly higher K level than the control)

Results and discussion

Leachate pH and electrical conductivity

In all columns, the leachate pH values remained at 6.5–7.8 throughout the experimental period (Fig. 1). In both Sai Keng and Shenzhen soil types, the columns treated with wastewater had pH values similar to the control (leached with seawater) in the first few weeks. But after the initial phase, pH of the wastewater treated columns was lower than that of the controls. The high ammonium content in the wastewater might cause nitrification which released H^+ and resulted a slight decrease in leachate pH. Leachate of Shenzhen columns had lower pH (around 6.8) than those of Sai Keng (around 7.2) in the first 3 weeks of study. From Week 3 onwards, pH of the Shenzhen leachate increased gradually and reached a level of 7.5 on Day 30. Thereafter, the leachate pH values of two mangrove soils were comparable.

The pattern showing the changes of leachate conductivity with experimental time was the same in all columns except that the Shenzhen ones had significantly higher initial conductivity values than those of Sai Keng (Fig. 2). The conductivity declined dramatically in the first 30 days, indicating the soluble salts of the mangrove soils were rapidly washed out. After this initial drop, the conductivity of all columns was maintained at around 10 mS cm^{-1}, with repeated cycles of slight increase and decrease throughout the rest of the study period. This suggests that the steady and equilibrium state of the soil column was achieved after 30 days leaching. In general, application of wastewater to

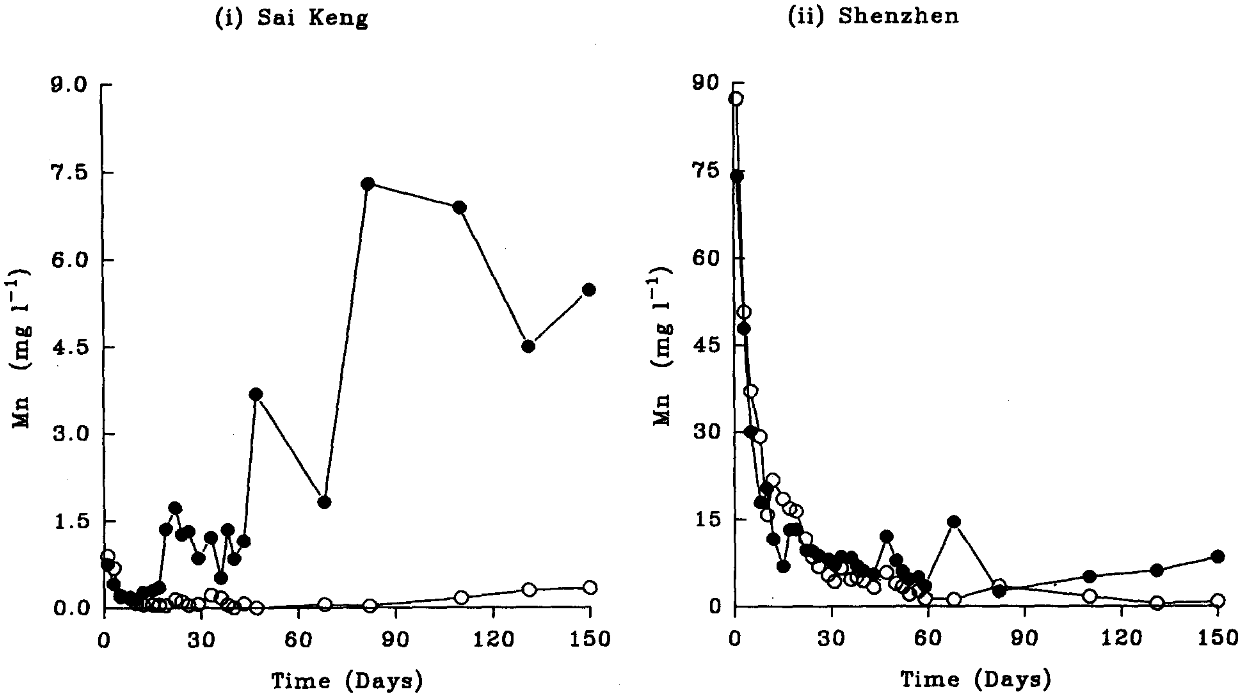

Fig. 6. Mn concentrations (mean of 3 replicates) of leachate collected from the control and treated columns of Sai Keng and Shenzhen soils. (o: seawater control; •: wastewater treatment; ANOVA results showed that the treated columns of Sai Keng had significantly higher Mn level than the control, but the Sai Keng soils had significantly lower Mn level than Shenzhen (note the difference in Mn scale between the two graphs), there was no difference between the treated and control columns of Shenzhen soil)

mangrove soil did not cause any increase in leachate salt content and there was no significant difference in leachate conductivity between the control and the wastewater treated columns.

Leachate inorganic nitrogen content

The NH_4^+-N concentrations of leachate collected from the control columns of both Sai Keng and Shenzhen soils decreased gradually with time and the NH_4^+-N content was less than 2 mg l^{-1} from Day 60 onwards (Fig. 3). This indicates that NH_4^+ originally bound to the soil especially the Sai Keng Mangrove was washed out rapidly by seawater. On the contrary, NH_4^+-N content of leachate discharged from columns treated with wastewater showed a gradual increase during the initial phase of the study. The initial ammonium rise period of Sai Keng wastewater treated columns lasted for about 35 days, reached a peak value of about 150 mg l^{-1}, then fluctuated at a level of around 130 mg l^{-1} throughout the rest of the experimental period (Fig. 3A (i)). The level was lower than that of the applied wastewater, indicating the mangrove soil had some capacity in immobilizing ammonium nitrogen. A similar pattern was found in columns of Shenzhen soil with two exceptions: (a) the initial phase of increase only lasted for 20 days and the NH_4^+-N concentration recorded on Day 19 was 78 mg l^{-1} (about half of that found in Sai Keng leachate); and (b) the NH_4^+ was maintained at around 75 mg l^{-1} after the initial rise, much lower than that of the Sai Keng columns (Fig. 3A(ii)). These results indicated that the Shenzhen columns reached the steady and equilibrium state more quickly than those of Sai Keng soil. Shenzhen soil also seemed to be more effective in retaining wastewater-borne ammonium as the leachate NH_4^+-N concentration was less than half of that found in wastewater (160 mg l^{-1} NH_4^+-N). Table 2 shows that about 40% of the added ammonium was immobilized in Sai Keng soil column while 58% was recorded in Shenzhen soils. The higher capacity of Shenzhen soil in trapping ammonium nitrogen may be because Shenzhen soil was more clayey than Sai Keng soil (Table 3). The former soil contained 55.5% clay while the latter only 11.6%. Shenzhen soil also had

Table 2. Nutrient budget of wastewater-borne N and P in column leaching study.

Treatment	Amounts of Nutrient Load		Amounts of Nutrient Released		Retention in Soil
	Wastewater (mg)	Soil(mg)	Leachate (mg)	Leached Seawater (mg)	(% of total nutrient added)
NH_4^+-N					
Sai Keng					
Control	ND	49.71	47.53	5.54	NC
Treatment	2048	49.71	1016.45	237.75	40.21
Shenzhen					
Control	ND	109.36	91.47	10.04	NC
Treatment	2048	109.36	766.79	143.51	57.81
NO_3^--N					
Sai Keng					
Control	ND	3.42	8.64	1.94	NC
Treatment	51.20	3.42	22.21	7.18	46.19
Shenzhen					
Control	ND	ND	13.80	4.01	NC
Treatment	51.20	ND	30.82	13.16	14.10
PO_4^{3-}-P					
Sai Keng					
Control	ND	26.40	1.66	0.21	NC
Treatment	512	26.40	1.32	0.21	99.72
Shenzhen					
Control	ND	133.34	1.61	0.56	NC
Treatment	512	133.34	42.39	7.17	92.32

(The nutrient budget was calculated based on the mean values of triplicate samples; ND: below the detection limits; NC: not calculated)

relatively higher cation exchange capacity (31.5 meq 100 g^{-1} soil). All these properties were in favour of the adsorption of NH_4^+ to the negatively charged colloids. The high organic matter content of Shenzhen soil (9.2%) might also explain its high NH_4^+ binding ability. Loss of wastewater ammonium through ammonia volatilization was unlikely in the present study because pH of the soil and leachate was not alkaline enough to stimulate volatilization.

Compared with NH_4^+-N, all leachate samples contained very low NO_3^--N content and nitrite was not even detected. During the first three months of study, the leachate NO_3^--N concentrations in all columns were maintained at relatively low values (< 2 mg l^{-1}) and the columns treated with wastewater had similar nitrate content to the control (Fig. 3B). This suggested that either nitrification was not significant or denitrification exceeded nitrification, or both. The mangrove soils, due to periodic flooding (wetting) and drying, were highly reduced and anaerobic which favoured denitrification. The high content of soluble organic carbon (glucose and peptone) in artificial wastewater further enhanced the efficiency of denitrification (Yamaguchi *et al.*, 1990). Moreover, the added glucose and peptone provided carbon and energy sources for heterotrophic bacteria and encouraged nitrogen mineralization and ammonification. The total heterotrophs were likely to have more competitive for limiting amounts of ammonium than autotrophic nitrifiers, and nitrifiers would probably have survived as viable inactive cells (Verhagen *et al.*, 1992). Figure 3B depicts that nitrate accumulated in leachate collected from wastewater-treated columns in the last two months and NO_3^--N concentrations of treated columns were significantly higher than that of the control, indicating that a certain amount of nitrification had taken place towards the end of the experiment. The nitrification was not steady, and large fluctuations in leachate

Table 3. General properties of mangrove soils.

Properties	Sai Keng	Shenzhen
pH	5.57 ± 0.09	5.39 ± 0.07
Conductivity (mS cm^{-1})	2.54 ± 0.06	4.33 ± 0.17
Texture: Sand (%)	73.65 ± 0.40	12.91 ± 0.21
Silt (%)	14.79 ± 0.43	32.41 ± 0.30
Clay (%)	11.56 ± 0.23	54.68 ± 0.33
CEC (meq 100 g^{-1} soil)	3.27 ± 0.16	31.50 ± 2.66
Nutrients		
Organic matter (%)	1.77 ± 0.07	9.16 ± 0.47
$NH_4{}^+$-N (mg Kg^{-1})	31.07 ± 0.80	68.35 ± 3.83
$NO_3{}^-$-N (mg kg^{-1})	2.135 ± 0.004	ND
Total N (%)	0.053 ± 0.002	0.173 ± 0.011
$PO_4{}^{3-}$-P (mg kg^{-1})	16.50 ± 4.57	83.41 ± 0.18
Total P (%)	0.019 ± 0.003	0.215 ± 0.012
Ext. K (mg kg^{-1})	11.35 ± 0.56	222.91 ± 14.36
Total K (%)	0.166 ± 0.02	0.79 ± 0.23
Heavy metals (mg kg^{-1})		
Ext. Cu	1.27 ± 0.11	1.56 ± 0.005
Total Cu	3.56 ± 0.36	8.28 ± 0.53
Ext. Zn	2.28 ± 0.09	15.92 ± 1.29
Total Zn	8.13 ± 1.02	63.15 ±11.41
Ext. Mn	2.81 ± 0.34	157.89 ± 7.59
Total Mn	10.70 ± 0.06	198.10 ±12.63
Ext Cd	0.08 ± 0.03	0.08 ± 0.04
Total Cd	0.25 ± 0.01	0.25 ± 0.06
Ext Ni	0.66 ± 0.05	1.30 ± 0.16
Total Ni	1.66 ± 0.16	10.86 ± 0.64

(mean and standard deviation values of 3 replicates were shown; ND: below the detection limit)

Table 4. Strength of artificial wastewater used in this study.

Composition	Conc. (mg l^{-1})	Composition	Conc. (mg l^{-1})
NH_4^+-N	160	K	200
NO_3^--N	4	Cu	4
organic N	48	Zn	20
PO_4^{3-}-P	40	Mn	20
TOC	320	Cd	0.4

$NO_3{}^-$-N content were also recorded. These findings suggest that nitrifiers might be able to establish their activities and populations within some oxidized micro-environment after a certain period of time. No major difference in nitrate level was found between Shenzhen and Sai Keng soil columns except that nitrification seemed to start earlier in the former soil type. When the nitrate budget was calculated, 29 mg nitrate was recovered in leachate from a total nitrate load of 55 mg in Sai Keng columns treated with wastewater. This indicates 46% of the nitrate was either retained in the soil or denitrified as N_2 or N_2O gases and released back to the atmospheric environment (Table 2).

Leachate phosphorus content

Figure 4(i) shows that in both control and wastewater treated Sai Keng columns, the $PO_4{}^{3-}$-P content was very low (less than 0.3 mg l^{-1}). Addition of wastewater containing 40 mg l^{-1} $PO_4{}^{3-}$-P to Sai Keng soil columns did not cause any increase in leachate ortho-P concentrations, indicating that the soil of Sai Keng was very effective in retaining wastewater P. More than 99.5% phosphorus in the wastewater was removed after percolating through Sai Keng soil, probably due to complexation with humic substances and physical/chemical adsorption on sites such as hydroxides and oxides of Al and Fe, carbonates of Ca and layer silicate minerals (Mansell *et al.*, 1985). Periodic flooding and drying of the soil might also increase a soil's P-binding capacity. The results also suggest that Sai Keng had very large capacity in trapping and immobilizing through-flowing P. The sorption sites of this soil type were not saturated with phosphorus even after 150 days of wastewater application.

A very different picture was recorded in Shenzhen soil columns. The P content of leachate collected from both seawater and wastewater columns remained very low (< 0.15 mg l^{-1}) in the first month but the P concentrations of wastewater treated columns increased rapidly from Day 24 onwards, reached a high value of 5.4 mg l^{-1} on Day 29, and thereafter fluctuated at a level of 4.5 ± 2 mg l^{-1} (Fig. 4(ii)). This level was much lower than the added wastewater P concentration (40 mg l^{-1}), indicating that although Shenzhen soil was less effective in immobilizing P than Sai Keng soil, over 90% wastewater P was bound in Shenzhen soils (Table 2). Pell and Nyberg (1989) employed sand-filters as wastewater purification systems and reported that the P adsorption process consisted of two phases: an initial phase during which all of the wastewater P was rapidly adsorbed to the soil particles, followed by a second phase characterized by less effective sorption. The lower P retention capacity of Shenzhen soil might be related to its high level of native P (Table 3). Differences in redox potential between Shenzhen and Sai Keng soil might also explain their difference in P-binding capacity: the former soil had higher redox potential. Patrick and Khalid (1974) showed that soils with low redox potentials could bind more P from soil solutions high in soluble PO_4^{3-} than could soils with high redox potentials.

Leachate TOC and K content

Leachate collected from Sai Keng columns had significantly lower initial TOC content than those of the Shenzhen leachate. A rapid drop of TOC was found in the first 30 days in all Shenzhen columns and the differences in TOC concentrations between the two soil types became less obvious from Day 30 onwards (Fig. 5A). The trend of TOC changes with experimental time was similar to that of conductivity values (Fig. 2). In both soil types, the TOC trend of the wastewater treated columns was the same as the control except that the treated ones had slightly higher TOC values from Week 4 onwards (Fig. 5A). The TOC content of the wastewater treated columns reached a low and steady state at around 20 mg l^{-1} towards the latter part of the study. More than 90% wastewater-borne TOC was removed by the soil mass. The added glucose and peptone of the wastewater might have been quickly degraded and utilized by soil microorganisms or adsorbed on the soil particles, as observed by previous studies (Gambrell *et al.*, 1987; Pell & Nyberg, 1989). A comparison of Shenzhen and Sai Keng leachate TOC concentrations indicates that the effectiveness of the two mangrove soil types in the purification of wastewater organic matter was similar.

Potassium, a mobile cation, was consistently leached out by seawater in the control columns of both Sai Keng and Shenzhen soils, declined from initial 260 mg l^{-1} to 40 mg l^{-1} in the first 3 months, and maintained at this low level thereafter (Fig. 5B). In both soil types, the columns treated with wastewater had significantly higher K concentrations in the leachate. After the early drop of potassium, the leachate K of the treated columns reached a steady level of about 180 mg l^{-1}, very similar to the wastewater K concentration (200 mg l^{-1}). This suggests that both types of mangrove soils were not effective in binding wastewater K. It has been reported that the K retained in the clay structure might have been expelled in the presence of NH_4^+ ions. Decomposition of organic matter and destruction of silicates through the action of organic acids might also release K from soil (DeBustamante, 1990).

Leachate heavy metal content

Heavy metals including Cu, Zn and Cd were not detected in any leachate samples, indicating the wastewater heavy metals were completely removed and immobilized in the soil mass. Previous studies have shown that soils of salt marshes were reduced and acted as sinks for heavy metals discharged from sewage effluents (Boto & Patrick, 1978; Harbison, 1986). In addition to physical adsorption on clay particles and chemical complexation on hydrous iron and manganese oxide, oxide formation is also important in precipitating metals from solution (Dunbabin & Bowmer, 1992). Cr, Ni and Fe could not be detected in any of the leachate either, indicating that the mangrove soils themselves were not contaminated. The only heavy metal detected in leachate samples was manganese. Figure 6 exhibits that the leachate of Shenzhen columns had very high initial Mn content (about 90 mg l^{-1}), which decreased rapidly in the first 2 weeks. The wastewater treated columns followed the same pattern and had fairly similar Mn values as the control, suggesting that Shenzhen soil was capable of retaining wastewater Mn. On the contrary, leachate of Sai Keng soil column started with very low Mn level but Mn concentrations increased gradually in wastewater treated samples (Fig. 6). Nevertheless, the Mn content of Sai Keng treated columns was comparable to that of the Shenzhen leachate, both having Mn concentrations lower than that of the artificial wastewater.

Conclusion

Mangrove soils are effective in removing TOC, P and heavy metals from wastewater of high strength. The columns reached steady state after some time of equilibration. Leachate samples collected from wastewater treated columns contained very low concentrations of PO_4^{3-}-P, TOC and heavy metals during the steady state. The reduction of wastewater NH_4^+-N was less satisfactory, and more than half of the wastewater NH_4^+-N were leached out from the columns. The degree of wastewater pollutant removal depends on the type of mangrove soil as the mechanisms involved in binding nutrients and heavy metals are significantly affected by soil properties, especially soil texture (the clay content), cation exchange capacity, contents of organic matter, carbonates, hydrous and oxides of iron, manganese and aluminium, and soil microbial activities. In the present study, Shenzhen mangrove soil was found to be more clayey. It had higher cation exchange capacity and contained more organic matter, phosphorus and manganese, and thus was more effective in retaining NH_4^+ than that of Sai Keng. On the contrary, Sai Keng soil had higher capacity in trapping P. In general, there is apparent difference between the two soil types in terms of wastewater TOC, K and Mn removal. Both soils had very high capacity in immobilizing wastewater-borne heavy metals. Metals such as Cu, Zn, Ni, Fe, Cr and Cd were not detected in leachate samples during the 150 days of experimental period. The only heavy metal found in leachate was Mn. Nevertheless, Mn concentrations of leachate collected from wastewater treated columns were very low although higher than those of the controls. These results indicate that discharge of wastewater containing high concentrations of heavy metals over a 150-day period did not cause any contamination problem in the effluent if the wastewater was percolated through the mangrove soil. However, the maximum capacity of the mangrove soil to retain wastewater-borne heavy metals and its long-term effects require further investigation.

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