Land and Water Resources Research and Development Corporation

MDR4

SUSTAINED PHOSPHORUS REMOVAL FROM SEWAGE BY ARTIFICIAL WETLANDS

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Final Report on LWRRDC Project MDR4

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1. ABSTRACT.

The short term capacity for phosphorus in planted artificial wetlands, and the equilibrium orthophosphate concentration in their effluent are determined by the sorptive potential of the gravel. The long term capacity is determined by the plants, which can have seasonal fluctuations in uptake. The speed of uptake to gravel is diffusion controlled. The major orthophosphate sorption sites are iron, associated with the biofilm. In reducing conditions when Fe(III) is reduced to Fe(II) the equilibrium orthophosphate concentrations rise greatly.

Suggestions for managing constructed wetlands so as to sustain maximal phosphorus removal are discussed in a separate confidential report.

2. ORIGINAL OBJECTIVES.

To contribute to the design of low cost, low technology, treatment of wastewater by planted, vertical flow wetland systems, and to the development of operational procedures for sustained effective phosphorus removal.

3. METHODS.

The establishment phase of the project involved evaluation of analytic methods; establishment of sewage monitoring; investigating hydraulics in pots of different shapes and the planting and growing of macrophytes. The hydraulic studies showed the slowness of thermal convection when mixing was desired, but the difficulty of avoiding it if plug flow were sought, so a successful method of forced convection using an external peristaltic pump was developed, for purposes of laboratory experimentation.

During this period the inadequacies (slow, unreliable, imprecise) of conventional phosphorus speciation via selective hydrolysates (APHA 1989) became clear and the use of a high performance liquid chromatograph (HPLC) was sought. Unfortunately, due to financial constraints, the necessary post column reactor on the machine was not installed until November 1992.

The second stage; determining the fates of orthophosphate in the rhizosphere, provided the key to phosphorus removal. Conventional analytical methods were used in mass balance studies to confirm the location of the phosphorus, and kinetic studies provided more information on phosphorus dynamics. Finally, chemistry of the substrate, especially the role of iron in phosphate binding, was investigated, using redox and extraction techniques. During investigation of orthophosphate uptake, it was found that analytic methods, that had been validated on synthetic and natural sewage, needed amendment to give accurate results with the outflows from experimental wetlands. The choice lay in the release of aquatic humic substances and iron from the wetlands which rapidly (1-12 hours) bound orthophosphate; suitable acidification (pH ca. 2) stabilised samples for several days, presumably by stabilising the iron as Fe(II) and inhibiting its catalytic oxidation of the organic matter (Stumm and Morgan, 1981). Total phosphorus digests (acid per sulphate method) needed post hydrolysates reduction with ascorbic acid to redissolve all orthophosphates.

Manipulative experimental work was carried out on 9 L and 25 L pots planted with the lake club rush, Schoenoplectus validus Vahl (A Love and D Love), in a washed river gravel from Wagga Wagga. The monitoring and loading trials at the Griffith sewage works used 0.39, 0.79 and 1.18 K L tanks; planted variably with S. validus; Typha orientalis Presl; Baumea articulata (R.Br.) S T Blake; and Cyperus involucratus Rottb. in the same gravel. This gravel had a mineralogic composition of > 95% quartz, about 4% albite and a trace of a mica and a clay mineral, and a bulk elemental ratio of Si(150); K(5); Al(9); Fe(0.13); R(O.01). Breen (1990) found it to have a surface elemental ratio of Si(150); K(123); Al(62); Fe(5); C(85). The Coffs Harbour pilot plant used a local gravel with mineralogic composition 60% quartz, 20-30% albite and < 20% of a mica, and a bulk elemental ratio of Si(150); K(15); Al(35); Fe(5) and P(0.17).

The third stage, to establish the fate of model poly- and organic phosphorus compounds in the rhizosphere, was held up by lack of the requisite HPLC equipment and, with the project ending 6 months early, was not addressed.

4. RESULTS.

4.1 Success of the project.

The three different aspects required for "... sustained effective phosphorus removal..." are the speed with which the phosphorus is removed from the influent; the mechanism of removal, since this determines the absolute maximum removal of the phosphorus; and the total (long term) capacity of the system for phosphorus.

The project has provided necessary understanding of mechanisms of orthophosphate removal. Factors influencing removal have been identified; removal paths have been quantified; and a model for orthophosphate removal has been proposed, which now provides a clear guide for management trials.
Specifically the project has met three aims:

**Aim 1:** "...to establish and quantify the changes taking place in the phosphorus pool and between the phosphorus pool and macro- and micro-biota in the vicinity of root zones of emergent aquatic plants".

Three factors control the major changes in the important orthophosphate pools in the rhizosphere. (Fig. 1)

![Diagram showing the interrelation of important orthophosphate pools in the rhizosphere](image)

The importance of the plants in maintaining the $\text{PO}_4^{3-}$ absorptive capacity of the experimental system was determined with mass balance studies at 30C on 9 L pots containing young plants and, at ambient temperatures, on 25 L pots with mature plants. The studies on the 25 L pots were carried out by K P Sharma (Sharma and Heritage 1982). The young, unharvested plants removed 38% of influent orthophosphate into above ground parts (Breen, 1980, found this value to be 40%). Summer and winter harvests of the plants in the 25 L pots yielded an above ground phosphorus load equal to 91% of influent phosphorus.

K P Sharma’s work also showed luxury uptake of phosphorus by *S. validus* in conditions of high availability of orthophosphate, with both elevated tissue concentrations, and continued uptake as plants developed, rather than through translocation of phosphorus already assimilated.

Experiments with the 9 L pots recorded 20% orthophosphate uptake by planted gravel, 30-40% by unplanted gravel which had received the same prior orthophosphate loading, and about 75% retention in fresh gravel. With low BOD synthetic sewage, 22% of influent orthophosphate was converted to non-reactive phosphorus (frP), 18% in mobile bacteria and 4% as filterable non-reactive phosphorus (fnP). The mass of fixed biofilm phosphorus was small (ca. 1%) and net rates of change were less than experimental error.

The initial rate of orthophosphate removal is essentially the sum of the gravel and plant uptake rates. It is greatly increased (up to 10-fold) by movement and mixing of the liquid in the rhizosphere. This is interpreted as a result of reducing diffusion path lengths and avoiding local depletions. The kinetics of the removal process during forced convection are higher than first order in orthophosphate, though not second order, and are only moderately increased with rising temperature (about 1% per °C) so the process is probably diffusion controlled, even with waste water circulation rates of 1 volume cycled every 1½ hours.

The rate of orthophosphate uptake by the plants is dependent upon their growth stage. During the period of slow growth (between seed set and new shoot growth), the rate was too low to distinguish it from gravel uptake. At times of large biomass increase the rates of plant and gravel uptake were equal. When rhizosphere orthophosphate concentrations fell, phosphorus moved from gravel to plants. This can only be expected to happen when the equilibrium phosphate concentration is greater than the minimum concentration the roots can take up.

The third factor identified as having major but very complicated effects on phosphate retention, or release, and on rhizosphere concentration, is the gravel and its biofilm. The gravel used in all Griffith work was delivered with a film of organic matter, iron and phosphorus. This phosphate was only reversibly extractable in acid or strongly reducing solutions. Freshly used gravels reversibly extract orthophosphate into water, as well as much more into acids or strongly reducing solutions. However a subsequent aqueous extraction of a gravel from which phosphate had just been extracted in reducing solution released more orthophosphate (5-10 times more) than after a previous aqueous extraction.

In experimental pots the effects of redox on phosphate release were also linked to the organic matter present, either from the plant roots and rhizomes or from influent BOD. In young planted pots, orthophosphate concentrations in the root zone decreased over several days towards a finite equilibrium concentration similar to that obtained with unplanted pots. Pots containing old roots and rhizomes (1 or more seasons) or after harvesting, or with high BOD, when loaded with nutrient also show initial decreases in orthophosphate concentration, but at later times (hours to days) several conflicting reactions occur. After the rhizosphere becomes reducing for iron ($E_{o} < 0.2 \text{ mg L}^{-1}$; $E_{x} 300-200 \text{ mV}$; Geltermann *et al.*, 1979) there is a large build up of phosphate and dissolved iron ([FeIII]), and of dissolved organic matter. Samples of this effluent, when removed for analysis, turn brown (1-12 hours), then precipitate, fixing most of the orthophosphate in this brown organic material. Because of these conflicting effects it was not possible to estimate an equilibrium orthophosphate concentration in older pots.
This behaviour has been observed in flood irrigated agriculture (Willett and Higgins, 1978) and natural wetland sediments (Holtan et al. 1988) and is generally attributed to specific sorption of orthophosphate to hydrous iron oxides by ligand exchange with aquo-, hydroxo-, or o1 groups. (Holtan et al. 1988), with the phosphate "ligand" more labile when the iron is in the ferrous state.

Reduction of Fe(III) hydrous oxides also acts in a compensating manner, by yielding Fe²⁺ (aq) ions, and poorly crystalline insoluble Fe(II) compounds, with greater surface area and more phosphate sorption sites. This reduced crystallinity persists for some time after reoxidation to Fe(III) hydrated oxides, while the free Fe²⁺ (aq) may reoxidize (to form another sorption site) some distance from its source (Holtan et al. 1988, Willett and Higgins 1978).

Hydrolysis of nrP by phosphatases associated with the biofilms of the Griffith pilot plant, loaded with primary settled sewage, were fast (Heritage pers. comm.). At 15°C and pH 7 complete hydrolysis of 400mg of nrP (equivalent to 1 EP or 200L⁻¹ of 2 mg L⁻¹ nrP) takes 12 minutes. Thus hydrolysis rates for the 20-50% of nrP in sewage are less likely to be limiting than is diffusion.

Aim 2: "... to identify and measure the effect of major factors controlling these processes and in scaled up trial systems at sewage treatment works".

Caution is needed in seeking to evaluate the relative importance of plant growth stage; rhizosphere hydraulics and the chemistry of the gravel biofilms in pilot plants. The pilot plant programs at Griffith and Coffs Harbour were implemented before the importance of these factors was identified, and were designed to monitor average outflow chemical characteristics. They only used weekly samplings, did not include macrophyte data, and were periodically interrupted by pump problems. Additionally the influent, primary settled sewage, is sufficiently complex and variable to obscure the basic chemistry.

Within these limitations, influents and effluents from the pilot plant wetlands at Coffs Harbour (Mitchell and Chick 1992) and Griffith (Heritage 1992) were spectrophotometric reactive and non-reactive phosphorus. During March and April 1992 phosphorus removal was reduced at both sites. At Griffith evapotranspiration was also less with three of the plant species showing lower orthophosphate removal. These results are consistent with the hypothesis of two major parallel phosphate removal paths, one of them being plant uptake during biomass increase, as late summer - autumn (after seed-set) is the time of slowed growth of field populations of many native macrophytes.

That diffusion controls gravel - orthophosphate sorption rates in the pilot plants can be inferred from the approximately 20% lower effluent orthophosphate concentrations of Breen (1980) and Sharma and Heritage (1992) (< 1 mg L⁻¹) using above ground buckets in which nightly mixing ("turnover") occurred, in contrast to the higher effluent orthophosphate at Coffs Harbour where there was negligible vertical cycling, and slow horizontal movement. Rhizosphere oxidation may also contribute to the effectiveness of small pot removal. The importance of rhizosphere oxidation in achieving low orthophosphate effluent concentrations was confirmed at the Griffith pilot plant when a trial with increased 24 hour draw-down resulted in effluent frP concentration falling from around 3 mg L⁻¹ to around 0.5 mg L⁻¹.

Other variables which may contribute to pilot plant performance, such as the effects of nrP compounds upon phosphorus removal, have not been examined, due to the lack of HPLC methodology, although in experimental systems the following have been observed:

within the range 5-7, pH did not influence orthophosphate uptake rates;

BOD only clearly influences orthophosphate uptake through its effect on redox potentials, but there was some evidence it also slightly increased the formation of npP. Its role in the biological hydrolysis of complex phosphorus was not assessed.

Aim 3: "... to establish phosphorus budgets for experimental and scaled up systems...."

The experimental budgets were described under Aim 1. Budgets have not been established at the pilot plants for the reasons described under Aim 2.

5. ADOPTION OF RESEARCH RESULTS BY THE WATER INDUSTRY.

While the objectives of this project were to gain an understanding of the basic processes involved in phosphorus transformation and removal in constructed vertical flowlands, the results of this work have direct application to the design and operation of these treatment systems. The availability of the information to government authorities involved in the treatment of sewage, run-off and specific industrial effluents will depend on successful commercialisation and technology transfer processes that now require discussion and action among CSIRO, who owns the relevant VFW technology, and its collaborators.
6. REFERENCES.

6.1 List of titles of publications arising from this and interacting projects.


Heritage, A D, Pistillo, P and Sharma, K P. Comparison of four emergent macrophytes in vertical flow wetlands used for sewage treatment. In preparation.


6.2 Other references cited.


7. SOURCE OF FURTHER INFORMATION.

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8. ACKNOWLEDGMENTS.

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