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Wetland treatment at extremes of pH: a review

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Abstract

Constructed wetlands are an established treatment technology for a diverse range of polluted effluents. There is a long history of using wetlands as a unit process in treating acid mine drainage, while recent research has highlighted the potential for wetlands to buffer highly alkaline (pH >12) drainage. This paper reviews recent evidence on this topic, looking at wetlands treating acidic mine drainage, and highly alkaline leachates associated with drainage from lime-rich industrial by-products or where such residues are used as filter media in constructed wetlands for wastewater treatment. The limiting factors to the success of wetlands treating highly acidic waters are discussed with regard to design practice for the emerging application of wetlands to treat highly alkaline industrial discharges. While empirically derived guidelines (with area-adjusted contaminant removal rates typically quoted at 10g Fe m^2/day for influent waters pH >5.5; and 3.5-7g acidity/m^2/day for pH >4 to <5.5) for informing sizing of mine drainage treatment wetlands have generally been proved robust (probably due to conservatism), such data exhibit large variability within and between sites. Key areas highlighted for future research efforts include: (1) wider collation of mine drainage wetland performance data in regionalised datasets to improve empirically-derived design guidelines and (2) obtaining an improved understanding of nature of the extremophile microbial communities, microbially-mediated pollutant attenuation and rhizospheral processes in wetlands at extremes of pH. An enhanced knowledge of these (through multi-scale laboratory and field studies), will inform engineering design of treatment wetlands and assist in the move from the empirically-derived conservative sizing estimates that currently prevail to process-based optimal design guidance that could reduce costs and enhance the performance and longevity of wetlands for treating acidic and highly alkaline drainage waters.

Keywords: wetland; acid mine drainage; alkaline filter media; passive remediation

1. Introduction

The use of wetlands is recognised as an effective remediation technology for a wide range of polluting effluents. These include long-established applications for secondary and tertiary sewage treatment (e.g. Vymazal, 2007), agricultural effluents (Borin and

Toccheto, 2007), urban runoff (Scholz, 2006) and circum neutral pH coal mine drainage (e.g. Hedin et al., 1994); as well as more emerging applications such as for the co-treatment of coal mine water and tertiary sewage effluent (e.g. Johnson and Younger, 2006). Wetland application in the wider paradigm of passive treatment, where remediation is undertaken through using only naturally available energy sources such as microbial metabolic energy, photosynthesis and topographical gradient (PIRAMID Consortium, 2003), has gained popularity with regulatory authorities and industry alike in recent decades due to cost savings and wider environmental benefits. These ancillary benefits include habitat creation, biodiversity and the inclusion of useable community green space in treatment system design (e.g. Greenway and Simpson, 1996, Kemp and Griffiths, 1999).

The buffering properties of wetland substrates have long been recognised (e.g. Ponnamperuma, 1972; Faulkener and Richardson, 1989; Dunbabin and Bowmer, 1992) and arise through several mechanisms. For alkaline influent waters, high partial pressures of carbon dioxide (pCO_2) in the wetland waters and substrates (e.g. Boyer and Wheeler, 1989; Schot and Wasssen, 1993), arising from both aerobic and anaerobic microbial respiration, depress pH and can also accelerate rates of calcium carbonate ($CaCO_3$) precipitation; a process which consumes alkalinity. Additionally, cation exchange and the production of organic acids can lower the pH of alkaline waters (Ross, 1996). In acid wetlands, the most important processes responsible for buffering waters are: (1) the dissolution of carbonate substrate materials, which generates alkalinity and consumes protons (equations 1 and 2) (2) the reduction of iron (Fe) hydroxides, which are abundant in terrestrial sediments (and ever more abundant in coal mine treatment wetlands: equation 3) and (3) bacterially-mediated sulphate reduction producing carbonate alkalinity in anoxic conditions (equation 4; Faulkener and Richardson, 1989; Younger et al., 2002).

$$CaCO_3 + 2H^+ \rightarrow Ca^{2+} + H_2O + CO_2 \qquad (1)$$

$$CaCO_3 + H_2CO_3 \rightarrow Ca^{2+} + 2HCO_3^- \qquad (2)$$

$$3Fe(OH)_3 + H^+ + e^- \leftrightarrow Fe_3(OH)_8 + H_2O \qquad (3)$$

$$SO_4^{2-} + 2CH_2O \leftrightarrow H_2S + 2HCO_3^- \qquad (4)$$

This review assesses recent progress in developing treatment wetlands for extreme pH wastewaters, assesses the performance of engineered and natural systems, and highlights gaps in understanding of wetland functioning at extreme pH. In comparing a relatively mature treatment technology (mine drainage treatment wetlands) with an emerging technology (highly alkaline treatment wetlands) the paper assesses how lessons learnt on system design and extremophile-mediated remediation processes at low pH can be used to inform studies and design of high pH treatment wetlands.

2. Acidic water treatment wetlands

2.1 Sources and environmental problems of acidic discharges

Acidic polluting waters are typically associated with drainage from abandoned coal mines. The acidic nature of the waters arises from the bacterially catalyzed oxidation of sulphide minerals (most commonly pyrite: FeS_2) (Equation 5), in flooded underground workings or surface waste rock heaps and tailings (Younger et al., 2002). When groundwaters containing ferrous iron (Fe^{2+}) released from pyrite oxidation discharge at the surface, the resultant oxidation to ferric iron (Fe^{3+}) (Equation 6) often results in rapid precipitation of ferric oxyhydroxide (Equation 7).

$$FeS_{2(s)} + 7/2O_2 + H_2O \rightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+ \qquad (5)$$

$$Fe^{2+} + 1/4O_2 + H^+ \rightarrow Fe^{3+} + 1/2H_2O \qquad (6)$$

$$Fe^{3+} + 3H_2O \rightarrow Fe(OH)_{3(s)} + 3H^+ \qquad (7)$$

Despite Equation 7 being a prolific producer of proton acidity, coal mine drainage in many areas tends to exhibit a bi-modal pH distribution (e.g. Kirby and Cravotta, 2005). Net-alkaline mine waters are often associated with Coal Measures strata receiving alkaline recharge, for example from carbonate-rich rocks, and possibly also as a result of incipient microbial sulphate reduction in the shallow sub-surface prior to surface discharge (e.g. Younger, 1995). Acidic discharges reflect a lack of buffering sources in the host geology.

The pyrite dissolution process is also responsible for the low pH sometimes found in discharges from abandoned metal mines, where pyrite is associated with the exploited mineral veins (e.g. Parkman et al., 1996; Naicker et al., 2003; España et al., 2005), ironstone mine spoil drainage (e.g. Heal and Salt, 1999) and weathering products of coal combustion residues (e.g. fly ash) derived from coals with a high sulphur content (e.g. Carlson and Adriano, 1993; Ye et al., 2001).

Acidic, ferruginous (Fe-rich) mine waters are a multi-factor source of pollution. Their principal source of degradation to surface waters is through smothering of benthic habitats by Fe oxyhydroxide precipitates (Jarvis and Younger, 1997). High acidity, salinity and concentrations of ecotoxic metals (e.g. Cd, Cu, Ni, Pb and Zn) associated with some mine water and coal ash discharges can also directly impact on aquatic biota (see Kelly, 1988).

2.2 Treatment options

A suite of active and passive treatment technologies have been developed in recent decades for treating drainage from abandoned mines. These include chemical dosing, the use of sulfidogenic bioreactors, limestone drains and permeable reactive barriers (for detailed reviews see: Younger et al., 2002; PIRAMID Consortium, 2003; Blowes et al., 2004; Johnson and Hallberg, 2005; Kalin et al., 2006). Constructed wetlands are one of the most widely used passive treatment technologies for addressing coal mine water pollution due to: (1) cost-effectiveness, (2) an excellent track record of success when designed in accordance with established guidelines (e.g. Hedin et al., 1994; Younger *et* al., 2002), (3) the capability to cope with changes in flow rates due to large storage volumes, and (4) the ancillary ecological benefits described in Section 1.

Since early observations of improvements in water quality from volunteer *Sphagnum* moss mires receiving coal mine drainage (Huntsman, 1978; Wieder and Lang, 1982), wetlands have been widely tested and deployed in the treatment of polluted mine waters. Despite concerns from some observers as to the effectiveness and predictability of wetland treatment of coal mine drainage (e.g. Wieder, 1989), which were largely related to inappropriate application of the aerobic wetlands at very low pH, aerobic wetlands have become very much an established technology for treating circum-neutral pH coal mine waters where Fe is the main pollutant of concern (Younger et al., 2002). These aerobic systems typically comprise a shallow (<0.3m) largely impermeable substrate of soil or clay planted with emergent macrophytes (Figure 1). At pH <5.5 the application of reducing and alkalinity producing systems (RAPS, or Successive Alkalinity Producing Systems (SAPS: Kepler and McCleary, 1994) – which comprise an unvegetated mixed bed of alkalinity generating media and organic matter, through which the discharge flows vertically through, sometimes also referred to as vertical flow wetlands) or compost wetlands (where site topography does not provide sufficient hydraulic head to drive waters through a RAPS) is typically recommended (Figure 1). Compost wetlands are constructed with a ~0.5m thick substrate of organic waste material (e.g. spent mushroom compost, manure, composted municipal waste) which promotes bacterial sulphate reduction in addition to producing alkalinity. Constructed wetlands are not however, the treatment *panacea* for polluted mine waters and may even be inadvisable where there are significant concentrations of xenobiotic metals (such as Hg and Cd). In addition, applications for removing mobile metals such as Zn are still problematic and usually require large wetland areas (e.g. Yang et al., 2006), while treatment of highly acidic waters remains challenging, as is discussed below.

A range of biogeochemical processes are responsible for attenuating mine water contaminants and generating alkalinity in wetlands (see Walton-Day, 1999). In aerobic surface-flow wetlands these encompass:

(1) formation and settlement of metal (primarily Fe) hydroxide flocs from suspension

(2) physical filtration of colloidal metal hydroxides from solution by plant shoots, roots and fibrous wetland materials (e.g. Burke and Banwart, 2002),

(3) direct uptake of metals into roots and shoots, which is particularly effective for low residual influent Fe ‘polishing’ wetlands typically deployed after preliminary settlement lagoons (Batty and Younger, 2002)
(4) iron plaque formation on roots and rhizomes of wetland macrophytes through oxygenation of the rhizosphere (e.g. Batty, 1999) and
(5) ion exchange and organic complexation.

In compost wetlands, the above processes will also be important (as compost wetlands will undoubtedly have strong redox gradients from oxygenated surface waters to deeper anoxic sediments), but removal of metals as reduced monosulphides (equation 4) and dissolution of primary carbonate minerals used in the substrate are also important processes harnessed for metal removal and alkalinity generation. The distinction between aerobic and compost wetlands can be somewhat blurred in reality given the sharp redox gradients that occur in wetland waters and substrates.

2.3 Wetland design guidelines and performance

2.3.1. Sizing metrics

There are several metrics that have been used for sizing and evaluating the effectiveness of mine drainage treatment wetlands in removing metals and acidity. These include the first-order kinetic model based on the oxidation of ferrous Fe proposed by Tartuis et al. (1999), volume adjusted contaminant removal rates (e.g. Manyin et al., 1997), but the design parameter most often used to size coal mine water treatment wetlands is the area-adjusted contaminant removal rate. This is typically quoted as the zero order rate in grammes per day per square meter of the wetland surface area at which the contaminant (most commonly Fe in aerobic wetlands or acidity in compost wetlands) is lost from solution (equation 8). Similar sizing protocols using equation 8 for various other metals / metalloids such as As, Mn and Zn are also being established for wetlands treating mine drainage and coal combustion by-product leachate, although removal rates are much slower than for Fe (see Hoover and Rightnour, 2002; Younger et al., 2002; PIRAMID Consortium, 2003). These are summarised in Table 1. This sizing criterion has the advantage of not assuming the constant flow rates, steady influent contaminant concentrations, plug-flow hydraulics and homogeneous contaminant removal across the wetland that are required for first order sizing expressions. In addition, while, the oxidation of Fe^{2+} is known to be first-order in Fe^{2+} concentration, the internal functioning of aerobic reedbeds depends on precipitation and sedimentation kinetics in addition to oxidation alone. Indeed, recent research has highlighted that while first order Fe oxidation kinetics do limit Fe removal in settlement lagoons, the settlement kinetics of iron flocs, which is zero-order with respect to Fe concentration, limit Fe removal rates in subsequent treatment wetlands where influent Fe concentrations are less (in the order of 30mg/L) (Hedin, 2008).

$$R_A = \frac{Q_d (C_i - C_e)}{A} \qquad (8)$$

A = treatment media area (m^2); Q_d = mean daily flow-rate (m^3/day); R_A = area-adjusted contaminant removal rate (g /m^2 /day).

Much of the initial progress in developing empirically-derived design rules for sizing coal mine treatment wetlands arose through work of the US Bureau of Mines in eastern USA (e.g. Hedin et al., 1994). The oft-quoted design rate of 10g Fe/m^2/day for aerobic wetlands and 3-7.5g acidity/m^2/day for compost wetlands (Hedin et al, 1994) have generally proved robust for the plethora of wetlands since commissioned using this guidance in the USA and UK (Younger et al., 2002). This robustness in design is largely a feature of the conservative nature of the design rate. This conservatism reflects the large variability in performance that was apparent in the relatively small sample data set from which the guidelines were formed (see Figure 2a). Performance variability is inherent in treatment wetlands due to deviations in contaminant removal temporally with ecoperiod, temperature and hydraulic and contaminant loadings in the short term. Over the longer-term changes in residence time that may manifest as a result of substrate accretion and development of short-circuiting can also diminish performance. While conservative design is beneficial insofar as it provides for flexibility in system operation (i.e. for variations in influent contaminant loadings), there are many cases where treatment wetlands operate far below capacity (e.g. Younger, 2004). Figure 2b summarises documented Fe removal rates for a range of mine drainage treatment wetlands in the UK highlighting that few achieve a 10g Fe/m^2/day removal rate, largely because in many cases additional land area to that suggested to be required by the above design criteria was incorporated into wetland design as a precautionary measure.

In addition to the variability in treatment performance in these early studies, the diminished Fe removal with lower influent pH was also plainly apparent (Figure 2a). This pattern is a feature of:

(1) inadequate alkalinity production to buffer the acidity produced from ferric iron hydrolysis (equation 7), which can lead to further lowering of pH and

subsequent increase in solubility of metals (e.g. Barton and Karathanasis, 1999; Whitehead et al., 2005),

(2) the slow hydrolysis of ferric iron to solid (oxy)hydroxides at pH<3 (Younger et al., 2002) which becomes predominantly a biologically-mediated process at pH <5, and

(3) reduced biological activity and plant performance (see Section 2.4).

As a consequence, wetland deployment for coal mine waters with pH<5.5 is typically recommended to incorporate anoxic limestone drains or alkali-dosing for pH adjustment of the waters prior to an aerobic wetland (e.g. Younger et al., 2002; Cravotta, 2003), or the deployment of a compost-based wetland or RAPS (Hedin et al., 1994; Klienmann et al., 1998) for influent pH > 4 but <5.5. The use of various configurations of treatment wetland types in passive treatment trains for the phased removal of different contaminants is common practice for some mine waters and coal combustion residue leachates (see Hoover & Rightnour, 2002; Younger et al., 2002).

2.3.2. Performance

The succinct illustration of diminished performance in aerobic wetlands at low pH provided by Figures 2a and 2b is supported by numerous observations of sub-optimal functioning and even failure of wetlands treating low pH and moderate (20-50mg Fe/L) to high (>50mg Fe/L) metal content mine drainage (e.g. Wieder, 1989; Barton and Karathanasis, 1999). While such patterns do not preclude the possibility of fairly high contaminant removal rates in aerobic wetlands treating net acidic influent waters (usually where influent Fe concentration is high – Figure 2b), the absence of alkalinity generation necessitates additional or alternative treatment efforts in most cases.

The success of wetlands treating acid influent waters depends critically on the development and sustained performance of suitable microbial communities in compost-based wetlands. The potential for harnessing sulphate reducing bacteria (SRB) in treating acid mine drainage has been long regarded (e.g. Tuttle et al., 1969). SRB perform the key terminal reductive step for metal removal (equation 4) which is rate-limited by the supply of carbonaceous organic matter degraded by primary heterotrophic bacteria (e.g. hydrolytic and fermentative bacteria). While early assessments suggested the diminished performance of SRB communities at $pH < 4$ (Hedin et al. 1994), the presence of acidophile genera of SRB has been found at various acidic mine waters in recent years (Johnson, 1998; Hallberg and Johnson, 2005). However, despite their perceived importance, there is generally no *a priori* design consideration of the microbial communities in compost wetlands, and in particular SRB; colonisation by the right microbial communities is assumed rather than designed for at present.

As such, the documented performance of compost-based treatment wetlands for acidic waters varies greatly. Heal and Salt (1999) document the effectiveness of a *Typha latifolia* compost wetland receiving ironstone mine spoil drainage in central Scotland. The total Fe removal rate was $0.8 g/m^2/day$ and treatment efficiency of 20-40% for acidity, Fe, Mn and Al. This sub-optimal performance was ascribed to slow rates of oxidation and precipitation of Fe and Mn given the low influent pH of 2.7. Later assessment of the same treatment system was undertaken by Woulds and Ngwenya (2004), and while they document evidence for bacterial sulphate reduction, similarly poor treatment performance was encountered due to the very high influent metal concentrations and low pH. At slightly less acid influent pH, deployment of compost wetlands has been found to be very effective. Younger et al. (1997) and Jarvis and Younger (1999) document the design and effective performance of a manure / municipal waste compost-based reedbed (with fly ash liner) treating coal mine spoil leachate (pH >4.5) in north east England. Total acidity removal rates of 10.4g/m^2/day were reported alongside evidence for immobilisation of metals as reduced monosulphides. Some of the inter-site variability in acidity removal rates at compost wetlands is summarised in Figure 2b.

Disparities in treatment performance of compost-based wetlands are also apparent over time at individual sites, with generally increased contaminant removal rates reported in summer months with increased biological activity (e.g. Heal and Salt, 1999). Some observers have also highlighted that the establishment of suitable microbial communities in wetlands and bioreactors receiving acidic drainage can be assisted by a suspension in flow of influent polluted water. Whitehead et al. (2005) highlight improved performance of anaerobic bioreactor treating acidic tin mine drainage at Cornwall UK after shut-down of the system for a period of months. Enrichment of active populations of SRB communities which developed in absence of the metal-rich (Fe >140mg/L; Al >45mg/L; Zn >80mg/L) low pH (<4) mine drainage was highlighted.

The longevity of compost wetland treatment (and more importantly microbial functioning) is a facet of system performance that can be overlooked in short term field and laboratory trials. In many wetlands and bioreactors the carbon source is initially present as labile cellulose-rich materials, leaving more recalcitrant lignindominated material for later breakdown which limits supply of low-molecular weight carbonaceous material to SRB communities (Pulles et al., 2004). The necessity for replenishment of the carbon source in compost wetlands has been long acknowledged (e.g. Kleinmann, 1990), but it is something that can often be neglected in full-scale system operation and requires further attention to develop sustainable strategies for attaining longevity of wetland treatment performance.

In addition to the uncertainties in predicting the effectiveness of microbially-mediated metal attenuation processes, the role of wetland vegetation and rhizospheral processes on metal mobility or retention is also crucial to treatment wetland performance. A review of such processes highlights that while changes in redox and pH in the rhizosphere may increase metal mobility in some cases, there is little evidence of widespread mobilisation of metals by wetland plants (Jacob and Otte, 2003). Jacob and Otte (2003) also highlighted the need for a better understanding of biogeochemistry of pore waters and seasonal effects of vegetation on metal solutes. Recent laboratory mesocosm studies have further stressed the importance of rhizospheral processes in mine drainage wetland performance, highlighting the buffering effects of the rhizosphere on microbial communities from toxic effects of elevated metal concentrations at low pH (Weber et al., 2007).

2.4 Vegetation of highly acidic aquatic environments

There are number of geochemical consequences of low pH within aquatic environments that can affect the growth of plants and other organisms. Firstly, acidity controls the speciation of metals within the aquatic environment, which often results in the presence of the free metal species more available to organisms. For example, aluminium largely occurs as the mononuclear Al species ($Al(H_2O)_6^{3+}$) at pH <5.0 and solubility is increased significantly (Ščaňcar & Milačič, 2006). The formation of iron plaques on the root surfaces as a result of oxygen diffusion from the plant roots and microbial activity has thought to prevent the uptake of metals into the plants through the processes of adsorption and co-precipitation (Greipsson & Crowder, 1992, Crowder et al, 1987) thereby providing an avoidance strategy for the plant. However, although some inhibition has been observed in wetland species, it appears that significant quantities of metals are still taken up into the plant tissues (Batty, 2005) and this has been implicated in the reduced growth of plant species in some wetland systems (e.g. Batty & Younger, 2004a; b).

The presence of elevated concentrations of H^+ ions within acidic environments not only poses a direct toxic threat to plant species, but may also interfere with nutrient uptake mechanisms. At low pH the efficiency of the H^+ efflux pump within the roots decreases and therefore can contribute to a decrease in the uptake of NH_4^+ (Yan et al., 1992). The uptake of inorganic N and growth inhibition has also been documented for Typha latifolia at pH 3.5 (Tolley-Henry & Roper 1986). Inhibition of both nitrogen and calcium uptake has also been implicated in the reduction of growth observed in Phragmites australis within wetlands receiving acid mine drainage (Batty & Younger 2004a).

Although acidic environments are usually considered to be stressful to plants, it has been suggested that although stress occurs as a result of changes in environmental conditions, once an organism has adapted to that situation it should no longer be considered stressful (Otte 2001). Previous research that examined populations of T.

latifolia (Ye et al. 1997) and Glyceria fluitans (McCabe & Otte, 1997) grown in metalliferous and non-metalliferous environments showed no difference in the tolerance to metal concentrations suggesting that stress does not occur as a result of high metal concentration (Otte 2001). It is likely that compartmentalisation of metals within the subcellular structures within the plants are a major effective strategy for avoidance of metal toxicity within wetland plants (e.g. Chabbi 1999). However, given metal toxicity has been implicated in the reduction of growth in plants receiving acidic metalliferous discharges (Batty & Younger, 2004a), further research to elucidate physiological and biochemical responses to metals and acidity would be beneficial.

Wetland plants have been shown to create large gradients in oxygen concentrations, pH and nutrient concentration within the rhizosphere (Marschner & Römheld 1983) and it has been suggested that a plant-induced increase in pH of the rhizosphere, through changes in the ratio of anion and cation uptake, could be a mechanism for tolerance in wetland plants (Brix et al 2002). It has also been suggested that the presence of iron plaques on the roots of wetland plants can act as a storage area for nutrients (phosphate is very strongly sorbed to iron hydroxides) and therefore plants can have a ready source of nutrients. Exudates released from plant roots may also be mineralised by micro-organisms thereby increasing the dissolved organic carbon beneath root plaques which can be recycled back to the plant (Chabbi et al 2001).

The vegetation within compost wetlands can provide a carbon source for the vital microbial communities involved in the removal processes and therefore it is advisable for these systems to be planted. While documented examples of the vegetation of compost wetlands are limited, there are numerous reports of wetland plant species growing in other highly acidic waters (see Table 2). These provide a potential range of taxa to use in compost treatment wetlands. One other important consideration in the growth of plants within acidic environments given the role they play as a carbon source is the decomposition of leaf material. Acidification of watercourses has been shown to result in a decrease in rates of decomposition (Burton et al 1985; Dangles & Chauvet, 2003) and this has also been observed in wetland systems for T. latifolia (Kittle et al., 1995). However, the decomposition of P. australis was not affected by acid conditions in experimental systems (Batty & Younger, 2007). Although many organisms responsible for the decomposition of plant material within neutral conditions may be negatively affected by acidic conditions, the presence of acid tolerant fungi (e.g. Gross & Robbins, 2000) and acid-tolerant bacteria (Reith et al., 2002) is likely to enable a certain amount of ecological redundancy within the communities. However, the extent to which carbon cycling is affected by acidity within treatment wetlands is still unclear and requires further investigation.

3. Alkaline treatment wetlands

3.1 Sources and environmental problems of highly alkaline leachates

Highly alkaline leachates can pose a threat to the aquatic environment from the weathering of several globally important industrial residues. These include steel slags (Roadcap et al, 2005), cement and lime spoil (Mayes et al., 2005), coal combustion residues derived from coal with a low sulphur content (Eary et al. 1990; Carlson and Adriano, 1993), Solvay Process waste (Effler et al., 1991), paper mill wastes (Phukan and Bhattacharyya, 2003), cementitous construction and demolition waste (Townsend et al., 1999) and oil shale leachates (Orupõld et al., 2000). The highly alkaline nature of these waters is typically related to the significant presence of lime (CaO) in source residues. The hydrolysis of lime (and calcium silicates) in the residues to portlandite ($Ca(OH)_2$) upon weathering and subsequent dissociation in solution, produces the hydroxyl ion (OH^-) which elevates solution pH (equation 9).

$$Ca(OH)_2 \rightarrow Ca^{2+} + 2OH^- \quad (9)$$

Alkaline leachates are of ecological concern to surface waters primarily due to excess rates of calcite precipitation as which armour benthic habitats downstream of disposal sites (e.g. Effler et al., 1991; Koryak et al, 2002). There are a number of other potential pollution concerns associated with highly alkaline drainage waters that are summarised in Table 3.

In recent years, there has been an increase in experimentation and deployment of highly alkaline industrial residues as filter media in treatment wetlands. These include blast furnace slags (Mann, 1997; Sakadevan and Bavor, 1998) and various coal combustion residues including fly ash (Drizo et al., 1999), flue-gas desulphurisation (FGD) by-product (Ahn et al., 2001) and hydrated oil-shale ash (Vohla et al. 2005; 2007; Kaasik et al., 2008), which have high phosphorus sorption capacities (see Table 4). The high Ca content of the materials provides various sinks for P, either co-precipitated or sorbed on the residues and secondary Ca-rich precipitates. These filter media are typically deployed in horizontal or vertical sub-surface flow wetlands to maximise contact of the wastewater with the media..

However, the deployment of such alkaline material in the substrate can hold issues for plant tolerance and be a source of highly alkaline effluent water from contructed wetlands (e.g. Ahn and Mitsch, 2001). In constructed wetlands deploying Filtralite-P^{TM} (a light weight expandable clay aggregate rich in Ca and Mg) and hydrated oil-shale ash (rich in hydrated Ca-phases such as portlandite, ettringite and hydrocalumite) as filter media, high effluent pH up to 10-12 (Ádám et al,. 2006) and 11 (Vohla et al. 2005; 2007) respectively has been documented. Such high pH will in most cases necessitate pH adjustment prior to discharge into surface waters.

3.2 Treatment options

Conventional management options for highly alkaline leachates are confined to direct chemical neutralisation, active aeration (e.g. Schramke, 1992; Roadcap et al. 2005), reciprocation of drainage waters over stockpiled or lagooned residues and natural attenuation through dilution and dispersal (e.g. Føllesdal, 2005). The former three of these options require a sustained capital input which may not be suitable at abandoned industrial facilities given the pollution problem can persist for decades (Matthews and Effler, 2003; Mayes et al., in press).

Recent research has highlighted the potential for wetlands to buffer alkaline lime spoil (pH up to 12.75) and steel slag (pH 12) leachates as a low-cost, passive approach to remediation (Mayes *et* al., 2005; Mayes et al., 2006). Similar to the early studies of mine drainage wetlands, these initial indications of the potential effectiveness of wetlands for buffering highly alkaline waters are provided by natural ‘volunteer’ systems. Mayes et al. (2006) assessed rates of buffering across a natural wetland in northeast England receiving steel slag drainage. Effluent pH was consistently <9 in the volunteer system with calcite precipitation rates (the process responsible for consuming sample alkalinity) up to twice peak values recorded in natural travertine precipitating waters (Dreybrodt et al., 1992). These rates were found to be highest in summer months in vegetated parts of the system where biological activity was significant (values between 7 and 14g day^{-1} m^{-2}; Mayes et al., 2006). High rates of calcite precipitation in wetlands can be a feature of (1) microbial respiration increasing carbonate concentrations (calcite precipitation being otherwise limited by carbonate availability), (2) the high specific surface area for precipitation provided by macrophytes, and (3) nuclei for precipitation offered by algae and other small organic debris which induce rapid loss of calcite from solution (e.g. Womble et al., 1996). The importance of biological activity in lowering the pH of highly alkaline effluents has also been noted by Orupõld et al. (2000) at lagooned oil-shale leachate operations.

Alternatively, the use of mineralised peat filters in sub-surface flow wetlands has been demonstrated to be effective in lowering pH of alkaline waters. In laboratory studies with artificial P-rich wastewater (Kõiv et al., 2008; Kirsimäe et al., 2008) and in pilot-scale studies treating P-rich landfill leachate and municipal wastewater (Kirsimäe et al., 2008), both using a hybrid system of horizontal subsurface flow (HSSF) filters filled with the hydrated oil-shale ash followed by vertical subsurface flow (VSSF) filters (laboratory) or HSSF filters (pilot-scale) filled with peat, the neutralization of high pH caused by dissolution of the ash-filters was significant (see Figure 3 for pilot-scale data).

3.3 Wetland treatment feasibility

3.3.1 Design guidelines

Given the embryonic nature of the research considering wetlands for treating highly alkaline drainage, there are as yet no clear design guidelines. Where the contaminants of concern have established wetland treatment guidelines, such as ammonia enrichment in Solvay wastes, then system design can be based on experiences in treating similar wastewaters (e.g. Kadlec and Knight, 1996). However, where the principal concern is high pH and carbonate crust smothering, the use of an area-adjusted calcite removal rate has been suggested as a suitable performance and design metric (Mayes et al., 2006). This rate can be calculated in a similar fashion to metal removal rates in mine water treatment wetlands using mass balance through equation 8, treating aqueous Ca^{2+} as the 'contaminant' and adjusting the removal rate to calcite through molar weight correction. Precipitation rates measured during the one year monitoring period of Mayes et al. (2006) were found to vary between 0.4 and 13.6g/day/m^2, although fairly consistent removal rates were reported over the study in the main body of the wetland (mean of 7.4 g/day/m^2 ± standard error of 1.1). There was also found to be a good agreement between rates estimated through mass balance and those measured directly. Lowest precipitation rates were recorded toward the wetland effluent (<5g/d/m^2), where pH was typically <9.5 and much of the calcite already lost from solution, and in leachate source areas (<2 g/d/m^2). These low rates in source areas were suggested by the authors to be a feature of limited carbonate availability in groundwaters upon emergence, given hydroxide dominates sample alkalinity at pH>12 and the slow conversion of $CO_{2(g)}$ to CO_3^{2-} is rate limiting.

3.3.2. System sizing

Unlike coal mine treatment wetlands where a target Fe concentration can be set (usually according to statutory quality standards: Younger et al., 2002), a defined target pH (given statutory demands for pH <9 in Europe at least) and calcite precipitation rate are required for alkaline treatment wetlands (as the main impact on aquatic biota is generally related to calcite smothering). Calcite precipitation rate however is not a parameter that is easily measured. Without an extensive database to inform how calcite precipitation rate varies with readily measurable parameters such as Ca^{2+} concentration and pH, a useful geochemical surrogate to use is that of calcite saturation index ($SI_{calcite}$). $SI_{calcite}$ describes the saturation of waters with respect to calcite on a log scale, with values in excess of +1.5 typically demanded for significant production of homogeneous calcite crystals in solution, while heterogeneous precipitation of calcite can occur at $SI_{calcite}$ >+0.3 (Ford and Williams, 2007). Calcite precipitation is sluggish at best at values of 0.0< $SI_{calcite}$ <+0.3 (Appelo and Postma, 2005), and of course non-existent for $SI_{calcite}$ <0. $SI_{calcite}$ values in the region of +2.5 at are common to highly alkaline waters (e.g. Mayes et al., 2006). A target effluent Ca^{2+} concnetration of 30mg/L has been used through rearranging equation 8 for preliminary sizing estimates by Mayes et al. (2006), who suggested this value corresponded with $SI_{calcite}$ <+0.3 (i.e. negligible calcite precipitation) and pH <9 at the site monitored. The projected sizes determined for a range of monitored leachate compositions were within the bounds of economic wetlands built for treating coal mine drainage (Younger et al., 2002). Clearly however, data from other high pH impacted wetlands (both volunteer and constructed) would be invaluable in quantifying inter-site and seasonal variability in calcite precipitation rates and also in developing empirical relationships between easily monitored parameters (e.g. pH and Ca^{2+}) and calcite precipitation rate.

3.3.3. Trace element dynamics in high pH wetlands

Secondary minerals, dominated by calcite precipitates, formed downstream of high pH calcareous discharges may assist in the immobilisation of some metals from solution through wetland systems. Sorption of divalent metals (e.g. Co, Mn, Ni, Zn) onto calcite has been widely documented in laboratory (e.g. Zachara et al., 1991) and field studies (e.g. Donahoe et al., 2004), and could provide an additional benefit of treatment wetlands at highly alkaline discharge sites where there is trace element concern. Studies on the permanence and bioavailability of any problematic metals accumulated in alkaline treatment wetlands would be desirable in assessing toxicity and sludge/substrate disposal options during system maintenance and renovation. Preliminary studies at a range of highly alkaline steel slag discharges suggests that rates of calcite precipitation are so high relative to trace element accumulation that actual concentrations of metals such as Cr, Ni and Zn in secondary precipitates are below sedimentary toxicity thresholds (Mayes et al., in press).

3.4 Vegetation of highly alkaline aquatic environments

The vegetation of wetlands at high pH serve similar functions to those at low pH, with flow baffling and provision of a large surface area for inorganic precipitates to be lost from solution. The principal role of macrophytes at high pH is however to provide a continued carbon source for the microbial decomposers responsible for elevating pCO_2 in the wetland. Non-saline high pH (>8) conditions are considered limiting to plant growth, primarily due to limited phosphorus (P) availability as a consequence of co-precipitation with calcite and Ca-Mg complexes (Bradshaw, 1983). There are a number of other potential direct and indirect nutrient cycling changes that can also be of significance to vegetation growth at high pH. These include (1) reduced solubility of micronutrients (particularly Fe, Mn, B, Zn and Cu; Brady and Weil, 1997), (2) reduced microbial activity, (3) reduced availability of potassium (Kinzel, 1983) and (4), direct toxicity of the OH^- (Rowell, 1988). Despite these potential limitations to growth, highly alkaline industrial residues have long been regarded as an important refuge for a diverse range of flora and fauna (e.g. Ash *et* al., 1994).

Recent work has highlighted similar spontaneous colonisation of highly alkaline aquatic environments by macrophytes at a range of sites in the UK (Mayes, 2003; Mayes et al., 2005; Mayes et al., 2006). Typical species found in highly alkaline wetlands are summarised in Table 2. Performance of Phragmites australis and Typha latifolia in highly alkaline media has been assessed relative to reference conditions in laboratory (Lawson, 2004) and field trials (Mayes, 2003; Mayes et al., 2005). Mean aboveground biomass in stands of T. latifolia growing in calcareous substrates receiving lime spoil drainage (pH up to 12.75) was observed to be less than 40% of that in an immediately adjacent reference site (Mayes, 2003). In laboratory tests on the comparative performance of P. australis and T. latifolia in calcareous substrates taken from two sites receiving high pH steel slag leachate versus control organic substrates, the impact of the alkaline media on plant growth was manifest in significantly reduced shoot production, shoot growth and higher root:shoot weight ratios (Lawson, 2004). The latter pattern was suggested in the study to be indicative of nutrient deficiency, as roots grow more in relation to shoots to seek out nutrients.

Micronutrient content of both highly alkaline and reference organic substrates were found to be similar in both field and laboratory tests suggesting the reasons for reduced performance to be due to significantly reduced N and P availability in high pH substrates (Mayes, 2003; Lawson, 2004). Significantly, organic amendments to the alkaline substrate were also seen to improve plant growth up to 6-fold (Lawson, 2004). The low organic matter content (and associated organic N and P pools) of substrates dominated by calcareous crusts and poor physical structure of carbonate rich sediments have been similarly documented to limit growth at Solvay waste-impacted sites (Auer et al., 1996; Madsen et al., 1996). Additionally, the formation of calcareous hardpans, which prevent root penetration when the substrate is not inundated, can provide physical constraints to plant growth (Mayes, 2003).

The use of highly alkaline industrial residues in constructed wetlands has been found to be of at least short-term significance to plant growth in some cases. Ahn and Mitsch (2001) document initially retarded growth of <u>Schoenoplectus tabernaemontani</u> in FGD-lined mesocosms, which was considered to be a feature of high pH (>10) of the liner leachate and potential elevations of boron early in the trials.

4. Research Needs and Conclusions

The biological and chemical processes that occur within wetlands have long been harnessed for treating polluted coal mine drainage waters. Diminished performance and occasional failure of wetlands treating extremely acid waters (pH <4) is ascribable to inadequate alkalinity generation, slower Fe hydrolyses and detrimental effects of elevated metal concentrations to some biota. These patterns prompted the widespread linking of wetland treatment with some form of pre-treatment (e.g. lime-dosing, limestone drains) or adoption of alternative treatment measures (e.g. RAPS) for very acidic influents. Highly alkaline leachates are produced from several globally important industrial residues. Evidence from volunteer wetlands has demonstrated the ability of simple surface flow wetlands to buffer high pH influent waters. Similar to coal mine drainage, the treatment process relies on mineral precipitation with biological activity and vegetation appearing to play an important role in improving performance. Unlike in acidic mine waters however, plant growth is not typically limited by toxicity, and options for overcoming the constraints to growth (macro-nutrient deficiency and physical properties of substrates) are readily overcome with suitable system design.

While there is evidence of diminished vegetation productivity at extreme pH compared to circum-neutral pH reference conditions (e.g. Batty and Younger, 2004b), clonal dominants such as Phragmites australis and Typha latifolia in particular have been documented to retain vigour, at both extremes of the pH spectrum. Wetland vegetation plays a crucial role in settlement and filtration of solid phase contaminants, uptake of contaminants in root and shoot material, oxidation of the rhizosphere and provides a large specific surface area for precipitation of solids from solution. In addition to this, successful propagation of vegetation in extreme pH conditions is essential for maintaining readily-available sources of carbon for microbial decomposers.

The evidence from acidic wetlands has shown the critical role of extremophile-mediated sulphate reduction, which is essential for the alkalinity generation and metal removal in compost wetlands (and even in some initially aerobic wetlands). Detailed inventories of the nature of these SRB communities have been made in various treatment wetlands (e.g. Hallberg and Johnson, 2005), but the design of compost-based wetlands and bioreactors at present is largely reliant on the assumption that SRB communities will develop given a suitable substrate and sulphate-rich drainage water. There is a clear need for obtaining a detailed understanding of the controls on the structure and functioning of these communities at different wetland sites and in controlled laboratory tests. Recent advances in microbial ecology such as the integration of molecular measurement methods (e.g. 16s rRNA) with ecological resource ratio theory and neutral community assembly models have been successfully employed in characterising and predicting microbial communities in other wastewater treatment settings (e.g. Sloan et al., 2006; 2007). These techniques and frameworks may provide the most suitable avenue for obtaining the necessary understanding to incorporate within mine water (and potentially alkaline leachate) treatment wetlands, opportunities for manipulating microbial community composition and resource provision during design or post-construction. The ability to do such will aid predictions of system performance, treatment longevity and could offer substantial reductions in full life-cycle treatment costs.

With alkaline treatment wetlands, the understanding of the role of microbial communities in the buffering process is at a far less advanced stage. Diverse microbial communities have been identified in extremely alkaline (pH 12) steel slag groundwaters (Roadcap et al., 2006) and the effects of microbial communities has been inferred in accelerating buffering in lagoons and volunteer wetlands receiving steel slag (Mayes et al., 2006) and oil-shale leachate (Orupõld *et al*., 2000). However, further efforts are required to understand the character, functioning and response of microbial communities at high pH.

Current design practice for coal mine drainage treatment wetlands is dominated by empirically-derived area-adjusted contaminant removal rates. These have by and large proved robust due to the setting of precautionary design guidelines prompted by the inherent inter and intra-site variability in removal rates. The understanding of microbial structure and functioning outlined above will assist in the longer-term move towards a process-driven basis to quantify and predict the biological, chemical and physical interactions that control contaminant removal rates at full scale for compost wetlands. In the interim, empirically-based guidelines could be improved through collation and thorough analysis of performance data from mine drainage wetlands in regionalised datasets. This will provide a basis for establishing the consistent relationships between performance parameters (e.g. hydraulic loading, influent concentrations, flow rate, removal rate, treatment efficiency) that are established for wastewater treatment wetlands (e.g. Kadlec and Knight, 1996) as well as offering a detailed evaluation of the performance longevity of treatment wetlands. Such datasets are currently being generated in Europe at least (e.g. PIRAMID Consortium, 2003). However, there are many operative treatment wetlands where crucial data (most commonly flow rates) are not routinely recorded.

At high pH, the understanding of the buffering process and design rates is at an embryonic stage. Further data on the effectiveness of wetlands in buffering highly alkaline waters (i.e. calcite precipitation rates and variability) from a range of sites is a must alongside the microbial community assessments discussed above. In conjunction with this, research priorities should also encompass an understanding of trace element dynamics and permanence of metal removal in highly alkaline wetlands.

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Table 1. Examples of documented pollutant removal rates associated with mine drainage and coal combustion by-product leachates in various wetland types (after Hoover & Rightnour, 2002 and PIRAMID Consortium, 2003).

Pollutant	**Type of wetland**	**Typical removal rate(s) ($g/m^2/day$)**	**Comments**	**Example references**
Acidity	Compost	3.5-7	Early assessment of range in performance from the USA	Hedin et al. (1994)
	Vertical flow (RAPS)	25-40	Note the increased effectiveness of RAPS systems	Watzlaf et al. (2003)
Al	Aerobic	0.1	Removal as a hydroxide occurs in both aerobic and anaerobic conditions. Far slower removal rates at low pH.	Hoover & Rightnour (2002)
	Vertical flow (RAPS)	1.7-3.2		Fabian et al. (2006)
As	Aerobic	18	Bacterially catalysed under acid conditions.	PIRAMID Consortium (2003)
Cd	Compost	0.02	Immobilised as reduced sulphide (greenockite; CdS) within anoxic substrate.	Ettner (1999)
Cr	Vertical flow (RAPS)	-	Conversion of hexavalent Cr to trivalent form	Hoover & Rightnour (2002)
Cu	Aerobic	0.05	Value from volunteer site so likely a minimum value.	Brown (1997)
	Compost	10	Cu removal likely to be as carbonate phase formed through reaction with respired microbial CO_2.	PIRAMID Consortium (2003)
Fe	Aerobic	10	Value typically quoted for net-alkaline waters.	Hedin et al. (1994)
	Compost	0.8	Acidic (pH<3) colliery spoil drainage	Heal and Salt (1999)
Mn	Aerobic	0.5	Alternative Mn oxidising bacteria systems achieve higher removal rates.	Hedin et al. (1994)
	Compost	0.01	Acidic (pH<3) colliery spoil drainage	Heal and Salt (1999)
Ni	Aerobic	0.04	Preliminary data.	Eger et al. (1994)
	Compost	2	Immobilised as millerite (NiS) in anoxic substrate	Ettner (1999)
Se	Aerobic	0.01	Se common to fly ash leachates	Hoover & Rightnour (2002)
U	Aerobic	0.1	Single value from volunteer site at Boršt (Slovenia)	PIRAMID Consortium (2003)
Zn	Aerobic	7	Aerobic reedbed with floating algal mats. Strong seasonal variations in performance. May be a net exporter in winter.	Kalin (1998)

Table 2. Documented species growing in extreme pH surface waters

Pollutant source	Documented species	Examples
Acid wetlands		
Coal mine drainage	Juncus effusus Phragmites australis Typha latifolia	Batty and Hooley (2005); Batty et al (2005)
Uranium mine drainage	Typha angustifolia Typha latifolia	Groudeva et al. (2004)
Metal mine drainage	Eriophorum angustifolium Phragmites australis	Batty et al. (2006); Hancock (1973)
Copper smelter drainage	Typha latifolia	Taylor & Crowder (1981)
Lignite mine drainage	Sparganium emersum	Sand-Jensen & Rasmussen (1978)
Mining lakes	Carex rostrata Juncus effusus J. bulbosus Schoenoplectus lacustris Typha angustifolia	Pietsch (1998); Chabbi (1999); Fyson (2000)
Alkaline wetlands		
Steel slag leachate / lime spoil leachate	Typha latifolia, Phragmites australis, Iris pseudacorus, Sparganium erectum, Carex flacca, C. nigra, Juncus effusus, Equisetum fluviatile, E. palustre	Mayes (2003); Lawson (2004); Mayes *et* al. (2005)
FGD by-product constructed wetland liner	Schoenoplectus tabernaemontani	Ahn and Mitsch (2001)
Solvay waste drainage	Phragmites australis Zanichellia palustris	Auer et al. (1996); Madsen et al. (1996)
Fly ash	Nyssa aquatica Phragmites australis Spergularia marina Typha latifolia	Shaw (1994), McLeod and Criavolo (1997)

Table 3. Examples of the pollutant concerns associated with different types of highly alkaline drainage waters.

Drainage water	**Potential pollution concern**	**Examples**
Lime spoil (Carboniferous limestone)	High pH (>11) and carbonate crust smothering	Andrews et al. (1997)
Lime spoil (Magnesian limestone) – active workings	High pH (>12), carbonate crust smothering, sulphate (from underlying Coal Measures strata)	Mayes et al. (2005)
Steel slag leachate	High pH (>12), carbonate crust smothering, Cr, V, sulphate	Koryak et al. (2002); Mayes et al (2006); Roadcap et al.(2005);
Solvay Process waste	High pH (>10), carbonate crust smothering, salinity, NH_3, NO_3, P	Effler et al. (1991); Effler and Whitehead (1996)
Construction and demolition waste	High pH (>12), salinity, sulphate, Fe	Townsend et al. (1999)
Coal combustion residues	High pH (>11), sulphate, salinity, Se, As, B	Spencer and Drake (1987); Eary et al. (1990); Besser et al. (1996)
Oil-shale leachate	High pH (>12), BOD, phenolic compounds	Orupõld et al. (2000)

Table 4. Documented phosphorus sorption capacities of various alkaline materials used in wastewater treatment wetlands.

Substrate	**Phosphorus adsorption capacity ($mg\ P\ g^{-1}$)**	**Example**
Fly ash	0.86	Drizo et al. (1999)
Steel slag	0.38	Mann (1997)
Blast furnace slag	0.40-0.45	Mann (1997)
Filtralite P™	Up to 4.5	Ádám et al. (2006)
Hydrated oil-shale ash	Up to 65	Kaasik et al. (2008)

Figure Captions

Figure 1. Simple schematic cross-sectional diagrams illustrating the type of treatment wetlands used for mine waters: a) aerobic wetland where emergent macrophytes are planted in a thin gravel substrate for net-alkaline ferruginous mine waters, b) compost wetland for acidic mine waters where head is limiting, c) Reducing and Alkalinity Producing Systems (RAPS) for acidic mine waters where there is sufficient head (after Younger, 2004). The latter are usually designed to remain unvegetated to prevent oxygen transfer via plant roots and rhizomes into the substrate. An alternative design of RAPS can incorporate a fully mixed layer of compost and limestone.

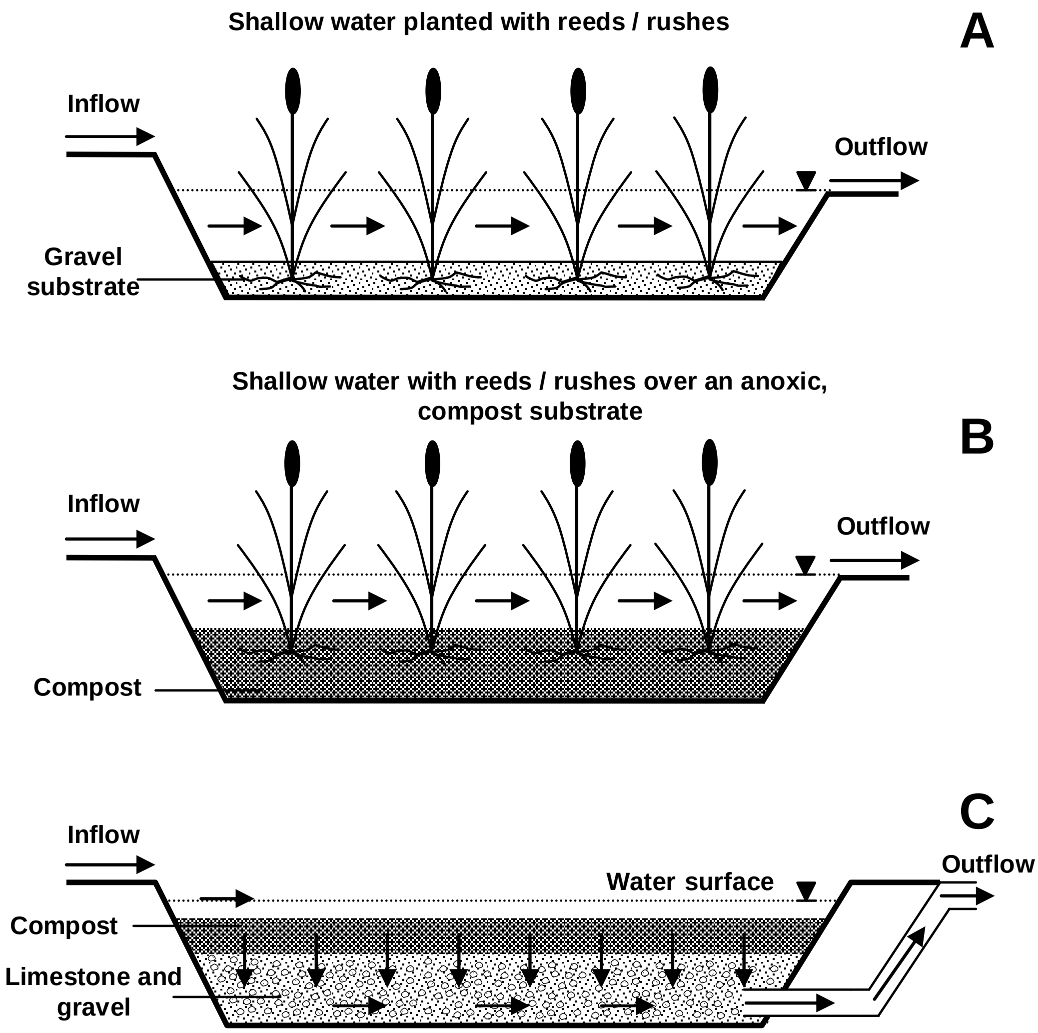

Figure 2a. Variations in mean area-adjusted Fe removal rate (with standard error of the mean displayed on *y* error bars) with influent pH from 17 treatment wetlands in eastern USA (after Younger et al, 2002). Figure 2b. Documented iron removal rates in various types of constructed wetland treating mine drainage in the UK. Data from: Younger et al. (2002); Brown et al. (2002); PIRAMID Consortium database (2003); Whitehead et al. (2005) and personal data of the authors. Triangles = compost wetlands, circles = aerobic wetlands. White fill = low influent Fe concentration (<10mg/L); Grey fill = medium influent Fe concentration (10 – 30mg/L); black fill = high influent Fe concentration (>30mg/L).

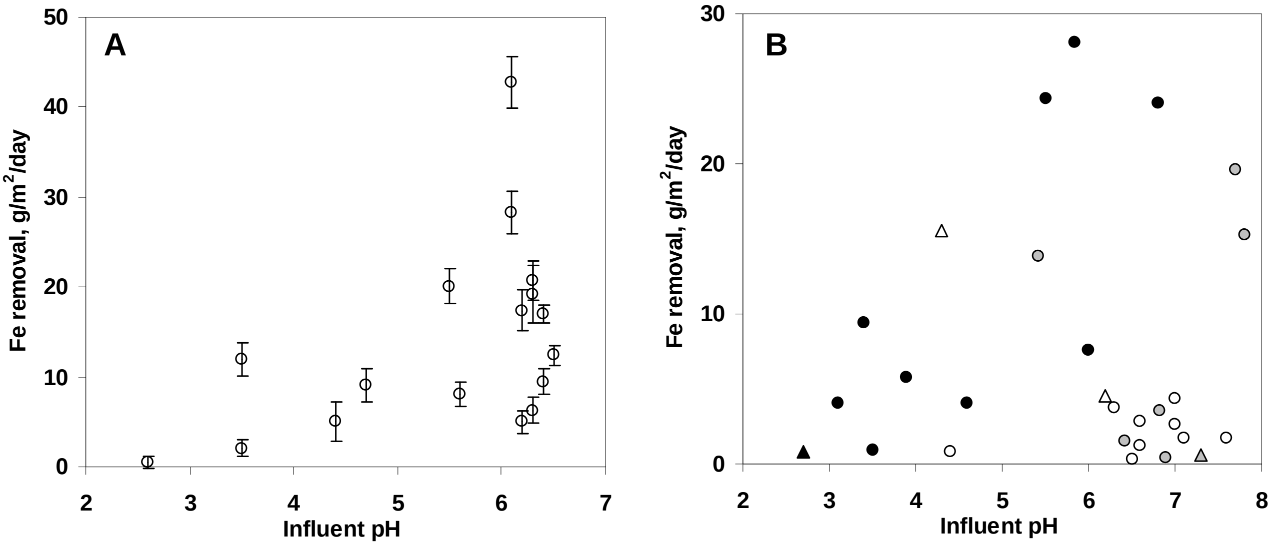

Figure 3. Mean values (n = 52) of pH in pilot-scale onsite experiments (September 2006 –September 2007) treating landfill leachate (Inflow 1) and municipal wastewater (Inflow 2); Ash 1 and 2 = effluent from horizontal flow hydrated oil shale ash filters; Peat 1 and 2 = effluent from horizontal flow mineralized peat filters. (After Kirsimäe et al., 2008).