The application of wetland technology for copper removal from distillery wastewater: a case study

C. Murphy, P. Hawes and D. J. Cooper

ABSTRACT

The ability of reed beds to remove significant levels of metals from effluent streams is well cited in the literature. Various methods of removal have been postulated and demonstrated including physical methods such as filtration and settlement, precipitation when the metal is present as a salt and adsorption to organic species or take up by macrophytes when the metal is in a soluble or ionic form. Consequently, reed beds have been used in a variety of applications for metal removal in water treatment processes. The distillation process for whisky generates an effluent containing a significant amount of copper which is scoured from the copper stills during the process and cleaning operations. High soluble copper concentrations can breach discharge consents. A horizontal subsurface flow reed bed system has been designed and installed for copper removal at a distillery in Scotland. This paper presents the findings of the literature search, outlines the design of the bed and reviews the performance results.

Key words | copper, distillery wastewater, metal removal, reed bed

INTRODUCTION

The ability of wetlands to remove metals has been widely studied in natural wetlands, constructed surface and subsurface flow systems and in laboratory scale wetlands, the results of which indicate their ability to act as sinks for metals with varying removal rates and efficiencies. The plant species, the substrate, the organic content, aerobic, anaerobic and anoxic zones all have roles in the removal pathways of heavy metals and the ultimate fate of metals (Lung & Light 1996; Mungur et al. 1997; Eger & Wagner 2003; Weis & Weis 2004; Murray-Gulde et al. 2005). The removal mechanisms taking place within the wetland are highly complex and can differ from one wetland to the next depending on the conditions within the wetland and the wetland type. Copper removal rates have been quoted as varying from 36.6 to 372.7 mg/m²/d (Mungur et al. 1997). This variability makes the design of a constructed wetland specifically for copper removal challenging. This paper will review the available literature with a view to utilising academic studies when determining design parameters for the practical installation of a reed bed treatment system.

Murray-Gulde et al. (2005) suggest that differences in the metal removal rates could be due to the specific design of the constructed wetland. Some studies rely on the harvesting of plants for metal removal (Lung & Light 1996; Cheng et al. 2002), others select plants to provide organic matter to act as a carbon source for sulphate reducing bacteria, or choose plant species specifically for their metal removing capabilities and tolerance. Deng et al. (2004) states that metal removal by wetland vegetation can be greatly enhanced by the judicious selection of plant species.

Studies to determine the fate and transport of copper in wetlands has focused largely on wetlands used for the treatment of acid mine water, and some on urban highway runoff (Mungur et al. 1995; Samecka-Cymerman & Kempers 2004).
Metal removal by wetlands

Wetlands are well known for their capacity to degrade organic substances and nutrients. Unlike organic pollutants, heavy metals are not degraded in biological processes, but they can be accumulated within the wetland using a variety of removal mechanisms (Cheng et al. 2002). The role of above and below-ground plant tissues and also the substrate in the removal mechanisms has been extensively studied. Murray-Gulde et al. (2005) determined the fate and transport of aqueous copper in a constructed wetland, and concluded that the copper is partitioning with all of the available organic and inorganic ligands present in the constructed wetland, not just those in the sediments.

The metal removal mechanisms are largely chemical in nature. Heavy metals are removed from the aqueous phase through adsorption, cation exchange and chelation with organic matter and sediments, adsorption to plant surfaces, uptake by plants and precipitation as sulphides and carbonates (Deng et al. 2004; Murray-Gulde et al. 2005).

Laboratory testing of metal removal by wetlands cannot be used as a precedent. All stages of lab scale wetlands are set up in a controlled environment. The results from such experiments may give an indication of the processes and removal mechanisms taking place, however they cannot be fully conclusive. Mungur et al. (1995, 1997) found that results from lab-scale experiments differed from similar experiments in a full-scale constructed wetland. Experiments by full-scale constructed and natural wetlands indicate that there are a number of processes taking place that are not yet fully understood. Mass balance experiments for copper removal by Murray-Gulde et al. (2005) found that whilst 61% of the influent copper was sorbed in the sediments, 7% sorbed by the plants, and 15% measured in the outflow of the wetland, 17% of soluble copper entering the wetland was unaccounted for. Weis & Weis (2004) identified that there was a further need for investigation into the role of symbiotic fungi and bacteria in the uptake of metals.

The role of plants

Macrophytes are known to assimilate pollutants in their tissues and provide a surface area and environment for microorganisms to thrive. Weis & Weis (2004) suggest that, within wetlands, the role of the plants in metal removal is that of phytostabilisation, where metals are immobilised and stored below ground in the roots and sediments, as opposed to phytoextraction, where plants act as hyperaccumulators and concentrate metals in above-ground tissues. These hyperaccumulating plants require harvesting and disposal to prevent the recycling of accumulated metals when the plants decompose. Exactly how and where these metals are stored within the plant has been the subject of many studies. Lesage et al. (2004) noted that individual macrophytes differ in the way that they affect the removal efficiency of heavy metals. There is good correlation between metal removal and root biomass. Mungur et al. (1997) and Cardwell et al. (2002) indicated that Typha latifolia had the highest accumulation of metal in the roots (14,168.7 µg compared with 2,092.8 µg in Schoenoplectus lacustris and 561.4 µg in Phragmites australis). This is due to the large root biomass of the Typha species. Metal accumulation varied within the actual plant, with the highest concentration in the root tip (top 5 mm) followed by the root, and then the rhizome. The lowest accumulations have been found in the above ground tissues. There is very little data on the phytotoxicity of macrophytes but it is generally considered that they are more resistant to heavy metal than terrestrial plants, however this varies between macrophytes species (Ye et al. 2003; Deng et al. 2004). Mungur et al. (1995) and Lee & Scholz (2007) indicate that heavy metal
tolerance exhibited by *Phragmites australis* suggests that mature specimens accumulate higher concentrations of metal than immature specimens and that growth does not appear inhibited when exposed to high concentrations. Mungur et al. (1995) also states that *Typha* ssp growing in heavily contaminated areas contained elevated levels of copper up to 256 mg/kg dry weight (DW) in the roots. Mungur et al. (1997) and Cardwell et al. (2002) suggest that *Typha latifolia* and *Schoenoplectus lacustris* are more tolerant to high metal concentrations than other species of macrophyte. Chandra et al. (2008) investigating the pre-treatment of Post Methanated Distillery Effluent (PMDE) with *Bacillus thurungiensis* in a biorector determined that the bacterial pre-treatment combined with a constructed wetland system greatly increases the overall bioaccumulation of heavy metals by plants.

Lung & Light (1996) considered the effect that litter has on the dissolved copper as a subsystem of the copper uptake process. Live biomass acts as a temporary storage medium for copper. Harvesting this biomass would remove the copper from the wetland system, thereby extending the life of the system for metal removal. This conflicts with Eger & Wagner (2003) who investigated wetland longevity and suggest that the litter plays a vital role in sulphate reduction as the organic matter provides a carbon source for the sulphate reducing bacteria to reduce sulphate to sulphide, and provides organic ligands for copper sorption; thus systems that are well vegetated can generate sufficient new removal sites.

Batty et al. (2002) noted that the pH of the wastewater affects the uptake of metals by plants with low uptake in acidic condition. Ye et al. (2003) identified that at high pH conditions, the root plaques enhanced copper uptake into the roots. Rhizocretions (Weis & Weis 2004) or root plaques are composed mostly of iron hydroxides and other metals such as manganese and aluminium that are mobilised and precipitated onto the root surfaces. Mungur et al. (1997) stated that both *Phragmites australis* and *Typha latifolia* form root plaques and that the removal of metals is due to adsorption and immobilisation.

### The role of the wetland matrix

Investigations of metal removal by wetlands has largely focused on uptake by plants. Lung & Light (1996) suggest that precipitation and sedimentation are the primary removal pathway for copper, with particulate copper held in greater amount in the sediments. Constructed wetland substrates vary from site to site but largely consist of either soil and/or gravel, whilst natural wetlands are entirely variable in composition, consisting of organic matter and mineral particles. Both natural and constructed wetlands contain aerobic and anaerobic zones within the substrate. Copper is held in anaerobic sites where the sulphide ion reacts with and retains the copper more effectively. Weis & Weis (2004) suggest that there is a higher concentration of metals in a reduced state in the anoxic/anaerobic zones and as such, the bioavailability of the metals is low compared with the aerobic zones. These reducing conditions limit the depth to which plant roots penetrate. This restricts the uptake of metals by plants to shallower conditions.

Vymazal (2003) and Lesage et al. (2004) concluded that metals were mainly removed in the first part of the bed near the inlet and this correlates with Murray-Gulde et al. (2005) who noted that the copper concentrations in the sediments and plants was not evenly distributed within the wetland, decreasing in concentration from the inlet to the outlet.

### Distillery effluent characteristics and treatment

The distillation process (as described in Skelton et al. 2001) has two stages. In the first wash distillation stage, the fermented liquor is heated and the alcohol is evaporated off. In the second stage, the alcohol moves into the second ‘spirit’ still where the process is repeated. The residue from the first distillation, known as ‘pot ale’, has a very low alcohol concentration (<0.1%) together with a high BOD concentration (>25,000 mg/l) and is strongly acidic (pH < 4). The residue from the second distillation, known as ‘spent lees’, has a BOD concentration of about 1,200 mg/l and contains virtually no alcohol (Skelton et al. 2001). The copper stills, and the high temperatures during the distillation process, result in some dissolution of the copper metal into the liquid contents. No soluble copper is found in the alcohol that goes to produce the whisky, but there is a quantifiable amount left in the ‘pot ale’ and the ‘spent lees’ wastes from each of the two stages. Typically, spent lees can contain copper at concentrations of 25–40 mg/l (Skelton et al. 2001).
Dufftown in Banffshire is a malt whisky distillery producing six million litres of whisky per year. Built in 1896, it is the largest distillery operating in the Diageo network of 27 distilleries and 2 grain distilleries in the UK. As with a large number of distilleries, Dufftown is located in a remote area and lacks access to mains drainage. Wastewater from the distillation process is sent to the on-site effluent plant (bioplant) for treatment before being discharged under consent to the River Dullan. The wastewater treated at the bioplant comes from three distilleries. It is pumped from the Dufftown Distillery and arrives in road tankers in from Mortlach and Glendullan distilleries for treatment.

Currently, the three distilleries are in operation 24 hours a day, 7 days a week and have periods of shut down during the year for cleaning and maintenance, although these are not synchronous. As a result, the bioplant at Diageo is run almost continuously to treat the effluent from these three distilleries. The combination of shut down events and the variability in the amount and composition of distillery wastewater results in daily and seasonal variations in treatment plant performance. The bioplant also acts to cool the distillery effluent which reaches temperatures of 35–40°C at the inlet to the bioplant.

Effluent from the distillery is pumped through a pH monitoring unit into a 250,000 litre balancing tank (Figure 1). Effluent containing caustic soda from the distillery cleaning process is pumped directly into a caustic tank which also contains effluent diverted from the balancing tank when the pH > 9. When the pH drops below 6.1 in the balancing tank, effluent from the caustic tank is drip fed back into the balancing tank to increase the pH to between 7 and 8, thereby diluting the caustic effluent. The bulk of the suspended solids in the distillery effluent settles in the balancing tank. From here the effluent is siphoned from the top and pumped into a 250,000 litre feed tank. The effluent flows from this feed tank into the first of two high-rate biotowers containing plastic media and this is followed by the first of two settlement tanks. Effluent from the first settlement tank is pumped into the second biotower and then through the second settlement tank. Sludge from the various stages in the bioplant is stored in a separate holding tank to be tankered away and, historically, the treated effluent was discharged into the river.

The average flow to the bioplant, using historical data, was determined to be 650 m³/d (7.5 l/s). Data provided by Diageo for the copper concentrations indicated an average soluble copper level of ~1.5 mg/l at the discharge point. With increasing restrictions on maximum consent values, Diageo required a final polishing stage to reduce the copper concentration to below 0.5 mg/l in the final effluent. A reed bed was installed to provide a low energy and low maintenance treatment system to achieve the revised discharge consent for copper.

Designing a reed bed for copper removal

As suggested by Lung & Light (1996) and Murray-Gulde et al. (2005), the assimilative capacity of copper by a constructed wetland is determined by the overall design, and the failure of wetland to meet discharge criteria is often due to poor design. Murray-Gulde et al. (2005) goes further and suggests that in order to achieve the design objective (that being copper removal as the primary function of the wetland), the constructed wetland's ability to remove metals relies on the removal of soluble copper from aqueous phase and partitioning to sediments in non-bioavailable forms.

Literary reviews indicate very little data that is specific to copper removal from distillery effluent. Copper removal rates for wetlands are variable due to the complex nature of the wetland type, the amount of oxygen available and the macrophytes used. Mungur et al. (1997) found copper removal rates varying between 36.6 to 372.7 mg/m²/d. This is a considerable difference in removal rates to be reliably used in the design of a reed bed whose specific function is for copper removal.

The literature review did provide an insight into the optimal conditions required for efficient removal of soluble copper (Lung & Light 1996; Mungur et al. 1997; Eger & Wagner 2003; Murray-Gulde et al. 2005). The reed bed requires both aerobic and anaerobic conditions not only for copper removal by adsorption and precipitation of sulphides, but also for BOD reduction (note that although the reed bed was not designed primarily to remove BOD, it is a consented requirement). The reed bed requires a substrate that supports precipitation and sedimentation and provides inorganic and organic ligands that can react with metallic species. The macrophyte most suitable for copper removal requires a high metal tolerance and a large root biomass.

Taking the literature reviews, flow data and effluent characteristics into account, a horizontal subsurface flow reed bed (Figure 2) was designed and installed at the Dufftown distillery bioplant as this system provides both aerobic and anaerobic zones. Effluent from the bioplant has a high flow rate of 650 m³/d. The substrate within the reed bed would need to be designed to have good hydraulic conductivity whilst providing the required conditions for copper removal. Gravel, rather than a soilbased substrate was chosen for this reason. The reed beds were planted with *Typha latifolia* for its tolerance to copper, and its large root biomass for the uptake of copper. Eger & Wagner (2003) determined that a site with aerobic and anaerobic conditions can exceed 25 years provided sufficient carbon is added to the system. There is no intention for the reed beds at Dufftown to be harvested as metal uptake into the above ground tissues is a small fraction compared to below ground tissues, and this will allow organic matter to remain in the bed to provide a carbon source for sulphate reduction.

The sizing of a reed bed can be a complex process, and is often determined, at least in part, by the available space and the specific parameter(s) that are required to be removed. The determining factor for the size of the reed bed at Dufftown was the minimum copper removal of 20 mg/d.
RESULTS AND DISCUSSION

The final design was a 2 cell lined horizontal subsurface flow reed bed which was installed and completed in July 2007. Effluent was pumped onto the reed beds soon after completion and the beds were initially flooded to allow the macrophytes to establish and to prevent grazing by rabbits. During this period the effluent flowed across the surface rather than down and through the media, resulting in erratic copper removal rates (see Figure 3). At the beginning of November, the water level was lowered to 50 mm below the surface, ensuring the influent has full contact with the media and growing biomass throughout the length of the bed. This produced improvement in the copper removal efficiencies. Average figures for the loading and performance of the bed are shown in Table 1.

Pot ale was accidentally introduced into the bioplant in June 2008 (see Figure 4). Pot ale is very acidic and as such ensures that any copper present would remain in solution. (Skelton et al. 2001). Generally, this is not an issue as the pot ale is tankered away to be treated separately, however, situations have occurred when tankers have not being cleaned out correctly and have introduced pot ale into the effluent treatment system, resulting in the death of the microbes in the biotowers. The pot ale contamination introduced a shock load to the reed bed and, coupled with the low pH, resulted in increased copper concentrations in the discharge effluent as seen in Figure 4. Diageo have recently taken measures to prevent this happening again by using a detection system that will shut down and prevent pot ale from entering the bioplant system.

The bioplant control system ensures that the pH of the distillery effluent going into the reed bed is between 7 and 8.5. It is therefore difficult to ascertain whether acidic conditions reduce the copper uptake by plants as described by Batty et al. (2002) and Ye et al. (2003) for this reed bed system. The effluent temperature entering the reed bed system is between 10 and 25°C, and discharges from the reed bed at around 9°C. Determining whether effluent temperature has any significance in copper removal in the Dufftown reed bed is difficult. Figure 5 identifies the removal of copper from the bed as a whole, rather than breaking it down into specific regions of the reed bed, and does not show any correlation between temperature and removal rate. This suggests temperature is not an

![Figure 3](https://iwaponline.com/wst/article-pdf/60/11/2759/447381/2759.pdf)

Table 1 | Average influent and effluent data for copper, flow, pH and temperature for the reed bed at Dufftown

<table>
<thead>
<tr>
<th></th>
<th>Surface flow</th>
<th>Subsurface flow</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flow (m³/d)</td>
<td>398 (48–687)</td>
<td>464 (158–861)</td>
<td>443</td>
</tr>
<tr>
<td>Influent temp (°C)</td>
<td>15.6 (11.7–21.3)</td>
<td>16.7 (10.2–24.7)</td>
<td>16.3</td>
</tr>
<tr>
<td>Influent pH</td>
<td>7.1 (6.8–7.9)</td>
<td>7.7 (6.5–8.6)</td>
<td>7.6</td>
</tr>
<tr>
<td>Effluent pH</td>
<td>7.1 (6.5–7.9)</td>
<td>7.6 (6.6–8.5)</td>
<td>7.5</td>
</tr>
<tr>
<td>Influent copper (mg/l)</td>
<td>0.46 (0.05–1.35)</td>
<td>0.28 (0.06–0.77)</td>
<td>0.34</td>
</tr>
<tr>
<td>Effluent copper (mg/l)</td>
<td>0.37 (0.08–1.05)</td>
<td>0.15 (0.02–0.55)</td>
<td>0.22</td>
</tr>
<tr>
<td>Copper loading (mg/m²/d)</td>
<td>220 (10–650)</td>
<td>160 (20–480)</td>
<td>180</td>
</tr>
<tr>
<td>Copper removal (mg/m²/d)</td>
<td>33 (–190.1–290)</td>
<td>75 (13–236)</td>
<td>61</td>
</tr>
</tbody>
</table>

Notes: Surface flow data is taken from the period July 2007 to November 2007 where the bed was operated in flood. Subsurface flow data taken from the period November 2007 to June 2008 where the bed was operated with flow 50mm below the surface. Figures in bold indicate the average for these periods, with the total average for the period July 2007 to June 2008. Figures in brackets indicate the minimum value and the maximum values.
important factor in determining the extent of copper removal in a wetland.

The hydraulic retention time for the reed bed is dependant on the flow. Using the design parameter of 650 m$^3$/d, the retention time was calculated to be 5 hours. However, the flow to the bioplant varies daily from 93 to 502 m$^3$/d (average flow during the study period 412 m$^3$/d) resulting in retention times varying from 4 hours (during periods of very high flow) to 22 hours (during periods of very low flow). Figure 6 shows copper removal as a function of retention time, with typical retention times of between 6 and 8 hours. There appears to be no correlation between retention time and copper removal rate.

Mungur et al. (1997) tested a lab-scale wetland with copper concentrations of 1, 5 and 10 mg/l achieving removal efficiencies ranging from 81.7% to 91.8%. Lee & Scholz (2007) were quoted as achieving 95.4 to 96.2% removal efficiencies once again, tested in a laboratory-scale wetland. Kadlec & Knight (1996) achieved removal efficiencies of 88% in a full-scale wetland treating inlet copper concentrations of 1.2 mg/l. The removal efficiencies at Dufftown are lower than these, achieving negligible removal when the surface was flooded, and ranged from 12.5% to 96% (giving an average of 47.7%) after the water was lowered below the surface interface (see Figure 7). Mungur et al. (1997) suggests that removal efficiencies increase as the inlet concentration increases. The inlet concentration at the Dufftown bioplant is relatively low, ranging from 0.05 to 1.35 mg/l. It is therefore difficult to determine from the data if copper removal efficiencies are increasing with increased inlet concentration to any great effect. The results, however, do clearly indicate an increase in removal rates when the water level was lowered. When the reed bed was flooded the removal rate was often negative (where copper in the discharge effluent exceeded the influent levels, suggesting that previously retained copper in the wetland may have been released), with an average of 33 mg/m$^2$/d ranging from 2190 to 290 mg/m$^2$/d (Table 1). After the water level was dropped to below the surface, the average removal rate was 75 mg/m$^2$/d, ranging from 13.1 to 236 mg/m$^2$/d.

Figure 4 | Expanded to show the soluble copper levels in mg/l using reed bed treatment showing both influent and effluent data. [B] indicates where water levels were dropped below the surface of the reed bed and [C] indicates the accidental introduction of ‘pot ale’ to the system.

Figure 5 | Copper removal (mg/m$^2$/d) compared with temperature (°C).

Figure 6 | Copper removal (mg/m$^2$/d) compared with retention time (hours).

Figure 7 | Copper removal efficiency (%) compared with copper loading (g/m$^2$/d) to determine if the copper loading has any influence on the removal efficiency.
CONCLUSIONS

Utilising academic studies for the practical design of a constructed wetland is challenging. Taking the data from one or several large or small-scale wetland studies and trying to emulate them in the design of a constructed wetland whilst anticipating similar treatment characteristics is not a reliable design concept. The results from lab-based studies, can vary considerably when compared with full-scale constructed or natural wetlands, as there are many variables (conditions, location, effluent constituents, macrophyte species, substrate etc.), that make individual and synergistic contributions to the overall treatment process. Nevertheless, studies on wetland capabilities for metal removal, either in the laboratory or on full-scale wetlands, are valuable because they investigate and provide a better understanding of the removal mechanisms involved, and provide an indication of the optimum conditions and preferred macrophyte species to achieve conditions for high metal removal/uptake. When designing a full-scale system, such optimum conditions should be taken into account. The reed bed system at the Dufftown Distillery bioplant was designed using these optimum conditions and it is now achieving the desired effluent concentrations for copper.

REFERENCES