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Technical Article

The potential use of exhausted open pit mine voids as sinks for atmospheric CO_2: insights from natural reedbeds and mine water treatment wetlands.

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Abstract.

Abandoned surface mine voids are often left to flood, forming pit lakes. These may lose much water to the atmosphere by evaporation (which may be a problem in areas with scarce water resources) and / or they may contain acidic and/or metalliferous water (a potential ecological problem, e.g. for migratory birds). Drawing simple but important lessons from experiences with compost-based passive remediation systems for acidic mine waters, an alternative end-use for open pit mine voids is proposed: gradual infilling with organic material, which can serve as a long-term sink for atmospheric CO_2, whilst ameliorating or eventually eliminating the issues of sustained evaporative water loss and / or acidic water pollution. Key to the success of this approach is the suppression of methane release from organic sediments flooded with sulfate-rich mine waters: the presence of even small amounts of sulfate (which is typically abundant in mine waters) totally inhibits the activity of methanogenic bacteria. Not only does this explain why studies of gas release mine water treatment wetlands never report methane emissions – CO_2 is the only greenhouse gas emitted, and this is clearly not at levels sufficient to undo the benefits of wetlands as net CO_2 sinks. While the compete infilling of open pits with organic sediments might take a very long time, only minimal maintenance would be needed, and if carbon trading markets finally mature, a steady income stream could be obtained to cover the costs, thus extending the economic life of the mine site far beyond cessation of mining.

Key words: after-use, bacteria, carbon, climate change, CO_2, compost, methane, lake, mine, pit, sulfate, wetlands

Introduction

Pit lakes have become one of the predominant after-uses for large open-pits after the cessation of mining activities. In some cases, pit lakes are being used as water supply reservoirs (e.g. Aguas Claras, near Belo Horizonte, Brazil; Sperling and Grandchamp 2008); others find recreational uses (e.g. flooded strip mine voids in eastern Oklahoma), or are nurtured as nature reserves. In the majority of cases, however, they are simply left as passive features in the landscape (Castendyk and Eary 2009)). In warm and dry climates this can be a liability for water resources, as much water is lost from pit lakes to the atmosphere by evaporation, thus consuming inflowing ground- and surface waters. This can be an important issue in the semi-arid and arid areas where many of the largest modern surface mines are found. The ecological value of pit lakes is somewhat undermined by their unnaturally high depth-to-surface-area ratios, which make most of them 'meromictic' in limnological terms (Castendyk and Eary 2009). Meromictic lakes are characterised by persistence of a deep water stratum, which remains aloof from seasonal turnover effects in the two overlying strata, and is thus generally rather cool, nutrient-poor and light-starved, thus limiting primary productivity by benthic algae. Steep pit walls tend also to limit their habitat values for many inland bird species, which typically wade water margins grazing benthic invertebrates. Furthermore, an estimated quarter of all pit lakes contain poor quality water, which is often acidic and/or metalliferous, due to leaching of contaminants from weathered rocks in and near the flooded void (e.g. Castro and Moore 2000). In particular, acidic conditions often make the metals Fe, Al, Mn (and less commonly also one or more of Pb, Cu, Cd, Ni, Zn and Se) more mobile and bio-available, resulting in an environment inhospitable for wildlife. Birds landing on contaminated pit lakes may thus be exposed to toxins (see, e.g., US Fish and Wildlife Service 2008), and may also bioconcentrate toxic metals and transmit them further up the trophic chain, far beyond the limits of the former mine site, when they become subject to predation. Finally, where pit lakes adjoin residential areas, they are often viewed as dangerous sites, as people falling into them often struggle to get out unaided due to the steep flanks. In densely-populated European countries, the traditional remedy for this problem was to infill open pits with municipal waste, eventually leaving a land surface restored to approximately natural contours. However, since the enactment of the European Union Landfill Directive in

1999, this option has been increasingly denied, at least for any pits that intersect the water table. Similar initiatives to increasingly divert waste away from landfills have been enacted elsewhere in the world too, usually driven by widespread concerns (albeit not always scientifically reasonable) over long-term groundwater pollution risks by leachate from deposited wastes. Where pit lakes are problematic (which, it is stressed, is by no means the case everywhere) and landfills are forbidden, is there a further alternative end-use that might be more acceptable environmentally?

This paper proposes such an alternative end-use. It draws upon the last two decades of experience with compost-based passive remediation systems for acidic mine waters to propose the gradual infilling of pit lakes (especially those with acidic / metalliferous water quality) to create long-term sinks for atmospheric CO_2. Key to this proposal is an understanding of the peculiarities of gas release from wetlands in general and mine water wetlands in particular, as well as issues of organic sediment accretion rates and the balance between aerobic digestion, compaction and water levels. These processes are considered in the following section, paving the way for the subsequent proposal of a pragmatic approach to the creation of pit lake carbon sinks. While the compete in-filling of open pits with organic sediments might take a very long time, only minimal maintenance would be needed, and if carbon trading markets finally mature, a steady income stream could be obtained to cover the costs, thus extending the economic life of the mine site far beyond cessation of mining.

Key processes

Are mine water treatment wetlands net sinks for greenhouse gases?

It seems like stating the obvious to claim that wetlands act as sinks for greenhouse gases, as they visibly accumulate organic debris from plants that grow by photosynthetic assimilation of atmospheric CO_2. However, the balance of gases entering and leaving wetlands includes an important subtlety that could mean that wetlands are not, in fact, net sequestrators of greenhouse gases: if they consume CO_2 only to release methane (CH_4), which is a far more potent greenhouse gas than CO_2, then despite their visible accumulation of organic matter, even a modest amount of this re-released as CH_4 could entirely undermine the climate benefits of the wetlands. (Incidentally, emission of N_2O and dinitrogen (i.e. gaseous molecular nitrogen, N_2) from wetland sediments would also represent greenhouse gas emissions, though the quantities are generally negligible). Just how much methane releases from wetlands can undermine their role as greenhouse gas sinks is demonstrated by the contrast in Global Warming Potential (GWP) of the two principal carbon-bearing gases: the GWP of CH_4 is approximately 23 times greater than that of CO_2 over a century (e.g. Smith and Wigley 2000). (While the mole-for-mole instantaneous infrared absorption rate of CH_4 is actually 25 times that of CO_2, the average residence time of CH_4 in the atmosphere is not as long as that of CO_2). That natural wetlands commonly emit CH_4 is well-known: spontaneous combustion of discrete pockets of methane degassing from marshes explains the nocturnal flashes of light that have become mythologised as “Will o‘ the Wisp” or “Marsh Sprites”. In recent years, several studies have aimed to quantify these fluxes from different wetland types in order to ascertain whether wetlands are net sources or sinks of greenhouse gases. The differing atmospheric longevities of CO_2 and CH_4 enter the reckoning in such studies, with, for example, Brix *et al.* (2001) suggesting that over short time scales (decades) *Phragmites australis* reedbeds may be regarded as net sources of greenhouse gases, whereas if carbon cycling is evaluated over longer timescales (>100 years), such reedbeds can be considered a net sink for greenhouse gases. More recently, a systematic review by Mitsch *et al.* (2013) suggest a timescale of 300 years before methane emissions become unimportant relative to carbon sequestration properties. Given the current predominance of greenhouse gases amongst the world’s environmental concerns, this conclusion is rather depressing for enthusiastic advocates (such as the present authors) of the restoration or replacement of the ravaged natural wetland systems of Europe and North America on ecological grounds(e.g. Erwin 2009;).

The above comments relate to wetland systems in general. How do they relate to wetlands receiving polluted mine waters? One of the principal characteristics of many polluted mine waters is elevated sulfate concentrations, typically derived from oxidative weathering of sulfide minerals (e.g. Banks *et al.* 1997). Even where the acidity yielded by pyrite oxidation has subsequently been neutralized (e.g. by carbonate dissolution), elevated sulfate concentrations typically persist, as the equilibrium solubility for the principal mineralogical control on dissolved sulfate (i.e. gypsum) is consistent with dissolved SO_4^{2-} of 2,000 to 2,500 $mg \cdot L^{-1}$ (the precise value depending on the cation composition of the water). Thus Nuttall and Younger (1999) reported voluminous discharges of calcium-sulfate facies water of circumneutral pH from limestone-hosted Pb-Zn-F orebodies in northern England, for instance. Now it has long been known that even very modest concentrations of sulphate substantially inhibit bacterial methanogenesis (Bryant *et al.* 1977; Conrad 1996). Even where microbial assays demonstrate the presence of some methanogenic microbes, these will not be producing significant quantities of methane if they are bathed in waters containing even just a few tens of $mg \cdot L^{-1}$ SO_4^{2-}. This explains the utter lack of any reports of methane emissions from mine water treatment wetlands. Although gas emissions are commonly observed in mine water treatment wetlands, particularly in the early stages of operation, when trains of gas bubbles often form conspicuous pock-marks in the sediment surface (e.g. Fig 1), repeated monitoring by the authors and their colleagues of such features in constructed wetlands treating mine waters in the UK has only ever revealed CO_2 and H_2S emissions.

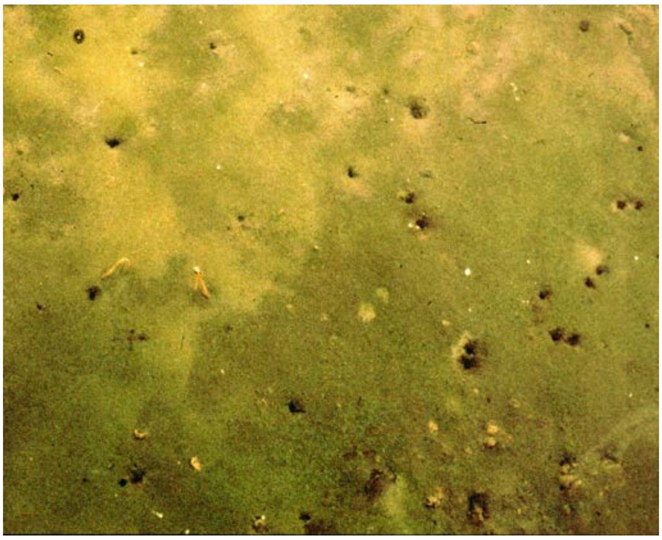

Fig 1 Pock-marks in sediment surface formed by gas release from a constructed compost wetland treating acidic colliery spoil heap leachate at Quaking Houses (Durham, UK) (width of field of view ~ 0.5m)

The evidence is thus that, because of the fact they receive large loadings of sulfate, mine water treatment wetlands stand somewhat alone amongst the wider spectrum of wetland types in that they tend not to release methane to the atmosphere. Thus most of the atmospheric CO_2 which they assimilate from the atmosphere either remains within the wetland sediment, with a modest amount being re-released in an essentially “carbon neutral” process. (Clearly ALDs and RAPS systems that include limestone dissolution in their repertoire of treatment processes will release some “fossil” CO_2 to the atmosphere, and this can be readily accounted for by a mass balance on dissolved Ca^{2+}).

Organic substrate accretion rates in wetlands

For wetlands to function as net accumulators of carbon, the sustained submergence of plant debris is essential: under sub-aerial conditions, microbial metabolism can swiftly return a significant proportion of the annual growth to the atmosphere as CO_2. Under the non-methanogenic subaqueous conditions to be found in mine water treatment wetlands, lingo-cellulose degradation is much slower, and much of the organic matter can survive with little alteration for extended periods of time. Evidence from natural wetlands shows that sustained saturation can easily preserve humified organic matter from wholesale oxidation for millennia, which in some cases will be long enough to ensure burial over geological time leading, eventually, to coalification. However, without manipulation of water levels, the natural tendency in a wetland basin is for accumulation of organic matter to lead to emergence of the sediment surface above the water line. Normally before this happens, littoral species will begin to invade the wetland, setting in train a sequence of events that is generally termed “hydroseral succession”. In natural systems, this begins with open lake water, which is first succeeded by reedbeds, then by willow carr, then by damp heathland and finally by grassland or woodland. In constructed wetlands left unmaintained, the usual succession would be from reedbeds to rushes, then to damp grassland. When designing mine water treatment wetlands (see, e.g., Younger *et al.* 2002), it is customary to incorporate as much freeboard (i.e. the difference in elevation between the initial water level and the crest of the retaining bund) as site topography will permit, to allow for build-up of organic sediment for many years before refurbishment of the system will be necessary. As there are few mine water treatment wetlands much older than twenty-five years as yet, published information on actual (as opposed to predicted) rates of organic sediment accumulation within such systems is as yet sparse. However, opportunistic refurbishment works at the Quaking Houses mine water treatment wetland (UK) in 2006 revealed an average rate of accretion over 8 years of 60 – 65 mm per annum (Jarvis, AP, personal communication, 6th December 2013).

Data on sediment surface accretion rates in natural wetlands are also rather sparse, despite an abundance of studies on biomass production rates. To compound the problem, published measurements of wetland accretion seem to be largely confined to estuarine wetlands (motivated by concern over loss of coastal habitat due to global sea level rise); unlike in mine water treatment wetlands, complex processes of subsidence / uplift and variable sediment inputs complicate the picture in estuaries. Such measurements as exist have typically been taken by gauging accretion relative to stable reference horizons or taking episodic readings from graduated stakes, moored in stable subsurface horizons. Additionally, ground survey measurement through standard surveying practices against known benchmarks or analysis and dating of sediment cores can be employed. Table 1 summarises reported wetland accretion rates. There is a clear need for better estimates of the rate of organic matter accumulation in reedbed wetlands as the small number of quoted values presented here vary over an order of magnitude. It is important to note that accumulation of plant debris and similar organic material is not the sole determinant of surface accretion in wetlands: clastic sediment inputs and in-wetland precipitaiton of various compounds also play a part. Mitigating against net accretion is compaciton of the accumulated sediment. Very few data appear to be available in the literature on this process. Borren *et al*. (2004) evaluated the role of compaction in peat deposits. They assumed that compaction leads to an increase in the dry bulk density over depth, with the deeper peat experiencing more pressure from the peat above and therefore undergoing more compaction. The conclusion to their work was that compaction is negligible in their study site in Siberia since they did not find an increase in dry bulk density. Other authors (e.g. Jauhiainen *et al*. 2004), however, have observed an increase in dry bulk density with depth.

A proposed process for redeveloping open pits as long-term carbon sinks

Armed with the foregoing insights into key processes, it is feasible to postulate an alternative decommissioning strategy for surface mine open pits which would essentially see them re-developed as long-term carbon stores. In essence, this requires controlling the rate and extent of post-mining flooding of such open pits in order to maintain conditions in which biomass may grow. Fig 2 illustrates the requirements. In order to commence the process of biomass production and hence the creation of a carbon sink, a pilot wetland must first be created in the base of the open pit. This can most conveniently be done shortly after the end of extractive activities by importing a growing medium, such as stored topsoil mixed with compost, which can then be seeded or (better) planted with seedlings of hardy, rapid-growing wetlands plants, such as *Phragmites australis, Typha* sp., *Iris pseudacorus*, and *Juncus* sp.. In many cases, it is possible to achieve much the same result by relocating sediments from ditches on the mine site in which such plants are already growing. Prior experience with wetland creation at UK mine sites has demonstrated the viability of this low-cost, low-fuss approach. Once a wetland has been established, the mine dewatering pump (which is here shown as a sump pump, though this would work equally well if external dewatering wells were used) is used to maintain the water level in the pit within an optimal range for wetland plant growth. In practice, this means that during the annual growing season the water depth needs to be maintained between 150 and 500mm above the wetland substrate surface: much shallower than 150mm and desiccation and invasion by terrestrial plants will occur, with elevated rates of CO_2 loss back to the atmosphere; much deeper than 500mm and even most wetland plants will struggle to grow, and might even drown if deep conditions persist for an extended period. In the season during which plants are dormant the water level may be increased in order to encourage collapse of emergent plant stems and leaves and their accumulation as sediment in the base of the pit. Although submergence by 2m is probably adequate for purposes of encouraging sedimentation of plant litter, the level of water may be allowed to rise by 6m or more above the surface of the growing medium. Increasing the depth of water above the surface of the growing medium reduces the requirement for pumping water from the pit at least temporarily; however, the deeper it is allowed to get, the greater will be the need for drawdown before the start of the subsequent growing season. (Incidentally, because

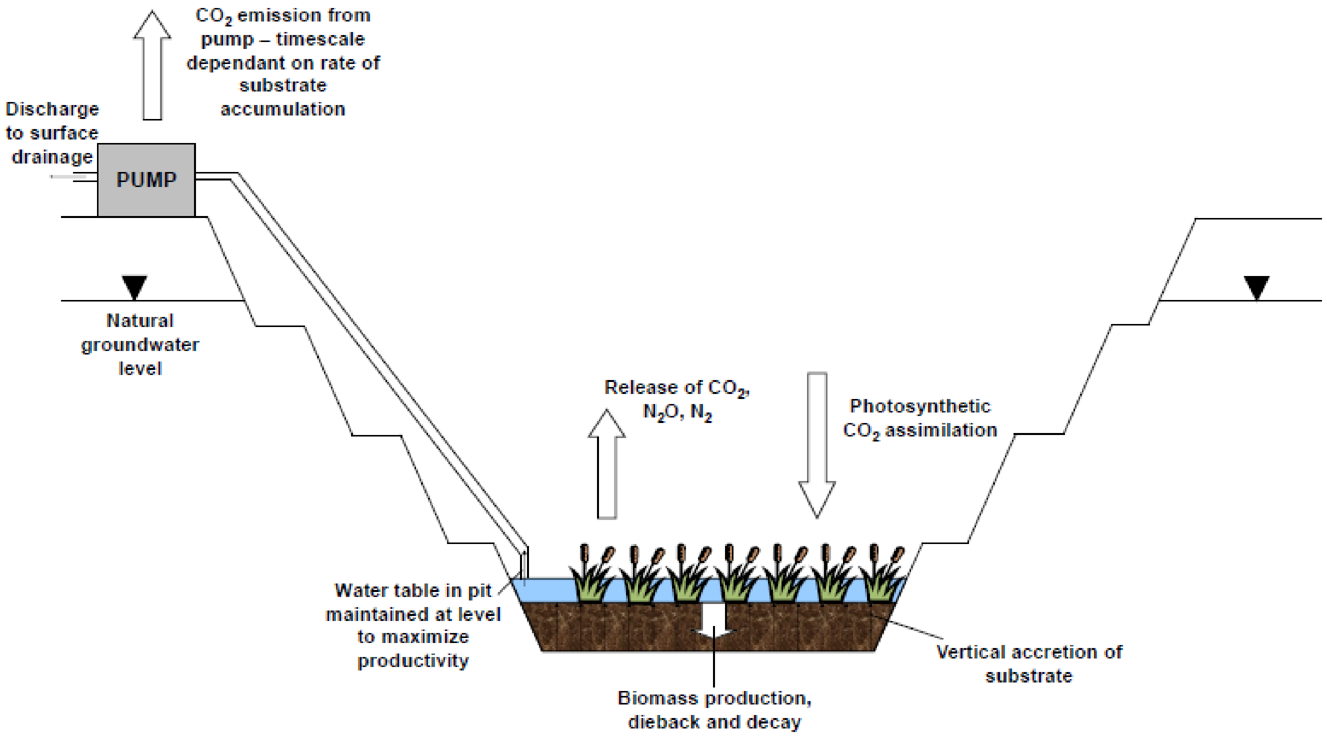

Fig 2 Schematic cross-section through a disused mine open pit being redeveloped as a carbon sink

the pit lake water will be passively treated whilst in contact with the organic fill in the void (see below), it is unlikely that pumped water will require extensive further treatment prior to off-sire disposal).

As plants grow each year, so does the sediment surface gradually accrete. In addition to the original material introduced to the base of the pit, the sediment now includes plant litter and other sediment (which may have been carried down to the floor of the pit by running water or the wind). As mentioned above, no further growing medium is intentionally added into the pit, but as the plants go through their growth and decay cycle sediment is created which advances up the pit. In effect there is additional growing medium in the form of sediment. The majority of plant roots are present in an upper layer of the growing medium of about one metre in depth. Whilst some roots do penetrate the growing medium to depths much greater than one metre, the growing medium behind the upper layer becomes a store of carbon rich biomass.

As the level of growing medium advances up the pit the seasonal minimum water level increase in tandem, until the surface of the sediment reaches some maximum level. Normally the maximum level will correspond to the natural water table level outside the pit. However, where the rock mass above the water table is of relatively low permeability, the process may be continued by adding water from outside the pit until the surface of the sediment reaches the top of the pit (or an even higher level if the pit is enclosed within an impoundment). Alternatively, the accumulated organic matter in the pit could simply be abandoned at any time, to be left behind as benthic sediment in a conventional pit lake.

The carbon sink consists of the organic matter deposited as the plants go through their growth cycle, which involves growth through photosynthesis, fixing of CO_2 from the atmosphere, and dying back in the winter, during which time carbon fixed in the plant materials is stored below the water level, where the bulk of it is preserved in solid form. For the types of plant used, there is no requirement to add further soil beyond that which is initially necessary to form the plant growth medium. As the volume of biomass advances up the pit, new plants grow in the organic matter residues left by dying plants. Pits left behind by surface mining are particularly suited to redevelopment as carbon sinks in this manner because of their depth (which is typically from tens of meters to a few hundred meters). This provides for the build-up of significant volumes of biomass before the sediment surface reaches the maximum level.

An advantage of applying the carbon sink formation process of the invention to abandoned surface mines is that the generated biomass is isolated from the external atmosphere by the walls of the pit on all sides and a body of water on the its upper surface. This guarantees long-term persistence of the accumulated organic matter in largely unoxidized form. Furthermore, as the volume of stored biomass grows, the biomass towards the bottom of the pit will be compressed by the weight of the overlying, younger biomass and the water, increasing the density of the deposit as a whole and thus the total mass of carbon that the pit as a whole can accommodate.

As previously noted, given the preponderance of sulfate in mine waters, methane evolution is not anticipated. Modest quantities of carbon dioxide may well be cycled back into the atmosphere whence they came, though the quantities in question are obviously very small in comparison to the amount of carbon remaining below the sediment surface. In order to qualify for carbon credits, however, sponsors are going to want some monitoring to demonstrate the lack of methane release, and to quantify the net loss of carbon from storage in the form of CO_2. Gaseous emissions could be readily quantified by means of periodic atmospheric monitoring above the pit surface, with the identified quantities being discounted from the total amount of carbon claimed as having been placed in long-term storage by means of organic sediment accretion. Table 2 gives illustrative examples of rates of release of greenhouse gases from other types of wetlands, listing only those which (like mine water wetlands) were observed to emit CO_2. As mine water wetlands are not expected to release CH_4, examples in which that was the only gas observed to be emitted have not been included. Table 2 represents a ready check-list of analytical techniques suited to performing the gas analysis that is envisaged to quantify the overall efficacy of the mine pit carbon sink proposed here. In addition to discounting greenhouse gas emissions, it would also be necessary to subtract the carbon emissions corresponding to the pumping used to control water levels.

An added advantage of this approach to after-use of open pits is the concomitant neutralization of proton and mineral acidity in mine waters by means of bacterial sulfate reduction within the body of accumulated sediment, just as occurs in RAPS and compost wetlands (see Younger *et al.* 2002). Not only will this mean that pumped water is unlikely to need further treatment (as noted above); it also means that any groundwater outflow from the pit will be of much higher quality than would otherwise be the case. Obviously, there are established alternatives for within-lake treatment of acidic pit waters, such as liming of the water body (e.g. Geller and Schultze 2013) or mixing with organic-rich sewage (e.g. McCullough *et al.* 2008). These approaches may well be more cost-effective than the method proposed here when the only aim is water treatment. However, liming involves applying a reagent that is derived from limestone by an industrial process that emits vast quantities of CO_2 to the atmosphere – the exact opposite of the main purpose of what we propose here. Hence, where it is desired to sequester CO_2 as an ecological / commercial exercise, and to end up with a restored land surface without resorting to landfilling of waste, then the method proposed here can achieve these ends whilst also treating the water.

There are three additions to the basic model outlined above that merit mention:

(i) Whilst in the simple example shown in Fig 2 the level of water in the pit is controlled by pumping, other suitable means of controlling the water level in the pit may of course be used. For example, in some pit environments it may be possible to control the water level by using wells to intercept groundwater before it can enter the pit, and / or by intercepting surface water inflows. Alternatively, for a pit on a hill or mountain, a tunnel or borehole directed horizontally into the pit from the side of the hill or mountain may be used to drain water and control the water level in the pit using a valve.

(ii) In certain geological settings a void may exist (or may be created) which does not intersect the water table. In low permeability rock, or with a suitable low-permeability liner (such as compacted clay, geotextile or other synthetic material) it would be possible to undertake the creation of a carbon sink by diverting other water into the void as needed to maintain the desired depth range above the sediment surface.

(iii) There is no particular reason why only plants grown within the void could be added to the carbon sink. Import of other sources of plant debris (e.g. lawn cuttings, chaff , woodland brashings etc) at the end of each growing season could be used to accelerate the overall rate of organic sediment accretion in the former open pit.

Clearly the entire process described above is dependent on the balance between the costs of maintaining the necessary pumping and the value of any carbon credits that can be sold on some functional carbon market. Unfortunately, carbon markets have got off to a very rocky start, with the earliest large scale example (the EU Emissions Trading System; see European Commission 2013) currently in the doldrums, following a collapse in the price of carbon emissions permits from more than €30 per tonne CO_2 equivalent in 2008 to less than €4 by the end of 2013. Nevertheless, carbon trading systems are gradually being introduced elsewhere in the world, and notably in countries with large mining industries such as Australia, China and Canada. Supposing these systems become firmly established, the process described above may well become a viable after-use for open-pit mine voids, making a contribution to the global search for decarbonisation technologies whilst eliminating a few longstanding headaches of the mining sector in the process.

Conclusions

Many abandoned surface mine voids are simply allowed to flood to form pit lakes. Some of these pit lakes prove to be liabilities, either in terms of public safety or environmental concerns (evaporative loss of water resources and / or exposure wildlife to acidic and metalliferous waters). While great advances have been made in the remediation of acidic waters flowing from abandoned mines, attempts to permanently remediate water within the open waters of pit lakes have generally been less successful. An alternative end-use for open pit mine voids as carbon stores, which coincidentally improve the quality of incoming groundwater / mine waste leachates is therefore a desirable development. Key to the success of this approach is the suppression of methane release from organic sediments flooded with sulfate-rich mine waters: the presence of even small amounts of sulfate (which is typically abundant in mine waters) totally inhibits the activity of methanogenic bacteria. While the compete infilling of open pits with organic sediments might take a very long time and require pumping to control water levels, only minimal maintenance would be needed, and if carbon trading markets finally mature, a steady income stream could be obtained to cover the costs, thus extending the economic life of the mine site far beyond cessation of mining.

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References

Banks D, Younger PL, Arnesen R-T, Iversen ER, Banks SD (1997) Mine-water chemistry: the good, the bad and the ugly. Environmental Geology 32: 157 - 174.

Borren W, Bleuten W, Lapshina ED (2004) Holocene peat and carbon accumulation rates in the southern taiga of western Siberia. Quaternary Research, 61: 42-51.

Brix H, Sorrell BK, Lorenzen B (2001) Are *Phragmites*-dominated wetlands a net source or sink of greenhouse gases? Aquatic Botany 69: 313-324.

Bryant MP, Campbell LL, Reddy CA, Crabil MR (1977) Growth of *Desulfovibrio* in lactate or ethanol media low in sulfate in association with H_2-utilizing methanogenic bacteria. Applied & Environmental Microbiology 33:1162–1169.

Castendyk DN, Eary LE (2009) Mine pit lakes: characteristics, predictive modeling, and sustainability. (Management Technologies for Metal Mining Influenced Water, volume 3). Society for Mining, Metallurgy and Exploration Inc., Littleton (CO). 304 pp.

Castro JM, Moore JN (2000) Pit lakes: their characteristics and the potential for their remediation. Environmental Geology 39: 1254-1260.

Conrad R (1996) Soil microorganisms as controllers of atmospheric trace gases (H_2, CO, CH_4, OCS, N_2O, and NO). Microbiological Reviews, 60: 609–640.

Darke AK, Megonigal JP (2003) Control of sediment deposition rates in two mid-Atlantic Coast tidal freshwater wetlands. Estuarine, Coastal and Shelf Science, 57: 255-268.

Erwin KL (2009) Wetlands and global climate change: the role of wetland restoration in a changing world. Wetlands Ecology and Management, 17, 71-84.

European Commission (2013) The EU Emissions Trading System (EU ETS). European Commission, Brussels. 6pp. (available on-line: http://ec.europa.eu/clima/publications/docs/factsheet_ets_en.pdf; last accessed 5th December 2013).

Geller W, Schultze M (2013) Remediation and Management of Acidified Pit Lakes and Outflowing Waters. Chapter 4 in Geller W, Schultze M, Kleinmann RLP, Wolkersdorfer CE (editors) Acidic Pit Lakes. The Legacy of Coal and Metal Surface Mines. 225 - 264.

Heinsch FA, Heilman JL, McInnes KJ, Cobos DR, Zuberer DA, Roelke DL (2004) Carbon dioxide exchange in a high marsh on the Texas Gulf Coast: effects of freshwater availability. Agricultural and Forest Meteorology, 125: 159-172.

Jauhiainen, S., Pitkänen, A. and Vasander, H. (2004). Chemostratigraphy and vegetation in two boreal mires during the Holocene. The Holocene, 14: 768-779.

Liikanen A, Huttunen JT, Karjalainen SM, Heikinen K, Vaisanen TS, Nykanen H, Martikainen PJ (2006) Temporal and seasonal changes in greenhouse gas emissions from a constructed wetland purifying peat mining runoff waters. Ecological Engineering, 26: 241-251.

Mayes, WM, Large, ARG, Younger, PL. (2005) The impact of pumped water from a de-watered Magnesian limestone quarry on an adjacent wetland, Thrislington, Co. Durham, UK. Environmental Pollution, 138: 444-455.

McCullough CD, Lund MA, May, JM (2008) Field-scale demonstration of the potential for sewage to remediate acidic mine waters. Mine Water and the Environment, 27: 31-39.

Mitsch, WJ, Bernal, B, Nahlik, AH, Mander, Ü, Zhang, L, Anderson, CJ, Jørgensen, SE, Brix, H. (2013) Wetlands, carbon and climate change, Landscape Ecology, 28: 583-597.

Nuttall CA, Younger PL (1999) Reconnaissance hydrogeochemical evaluation of an abandoned Pb-Zn orefield, Nent Valley, Cumbria, UK. Proceedings of the Yorkshire Geological Society 52: 395 – 405.

Rooth JE, Stevenson JC (2000) Sediment deposition patterns in *Phragmites australis* communities: Implications for coastal areas threatened by rising sea-level. Wetlands Ecology and Management, 8: 173-183.

Rooth JE, Stevenson JC, Cornwell JC (2003) Increased sediment accretion rates following invasion by *Phragmites australis*: The role of litter. Estuaries, 26: 475-483.

Smith SJ, Wigley TML (2000) Global warming potentials, 2: Accuracy. Climate Change 44: 459–469.

Song CC, Yan, BX, Wang YS, Wang YY, Lou YJ, Zhao ZC (2003) Fluxes of carbon dioxide and methane from swamp and impact factors in Sanjiang Plain, China. Chinese Science Bulletin, 48: 2749-2753.

Sperling EV, Grandchamp CAP (2008) Water quality of a deep pit lake: case study of Aguas Claras, Brazil. In: Rapantova N, Hrkal Z, (editors) Mine Water and the Environment. Proceedings of the 10th International Mine Water Association Congress, Karlovy Vary, Czech Republic, 2nd – 5th June 2008. pp. 615 – 618.

Stadmark J, Leonhardson L (2005) Emissions of greenhouse gases from ponds constructed for nitrogen removal. Ecological Engineering, 25: 542-551.

Teiter S, Mander U (2005) Emission of N_2O, N_2, CH_4 and CO_2 from constructed wetlands for wastewater treatment and from riparian buffer zones. Ecological Engineering, 25: 528-541.

USDA (2001) Constructed wetlands. United States Department of Agriculture, Natural Resources Conservation Service. Report NEH-637-03.

US Fish and Wildlife Service (2008) Region six environmental contaminants - Pit Lakes. (Available at www.fws.gov/mountain-prairie/contaminants/contaminants8.html; last accessed 5th December 2013).

Younger PL, Banwart SA, Hedin RS (2002) Mine Water: Hydrology, Pollution, Remediation. Kluwer Academic Publishers, Dordrecht. (ISBN 1-4020-0137-1). 464pp.

Zedler JB (2000) Progress in wetland restoration ecology. Trends in Ecology & Evolution, 15: 402-407.

Table 1. Published values for vertical accretion rates of sediment surfaces in natural wetlands.

Site	Accretion rate	Comments	Reference
Brackish tidal wetland, Chesapeake Bay, Maryland, USA.	40-62mm/yr (non-*Phragmites*); 95mm/yr (post-*Phragmites* invasion)	Comparison of accretion rates (through Pb dating of sediment cores) in stands affected by *Phragmites* invasion and reference populations.	Rooth *et al.* (2003).
Brackish tidal wetland, Chesapeake Bay, Maryland, USA.	Up to 128mm/yr in *Phragmites* stand	Measured using reference (feldspar) marker horizons. Marine sediment accretion in addition to accumulation of plant organics. Seasonal events a major control on accretion.	Rooth and Stevenson (2000)
Generic guideline	130mm/yr	Generic estimate for constructed wetlands used for animal waste treatment. Very high suspended solids likely to be a major control on accretion rates.	USDA (2001).
Gleason and Walkerton Marsh. Tidal riparian marsh.	Up to 300mm/yr	Measured using reference (feldspar) marker horizons. Vegetation predominantly freshwater marsh species. Marine and fluvial sediments an important control on accretion rate.	Darke and Megonigal (2003)
Magnesian limestone quarry settlement ponds, Co. Durham UK.	Up to 90mm year	Measured using fixed sedimentation rules. Combination of suspended solids and organic accretion in *Phragmites ausralis* reedbeds.	Mayes et al. (2005)

Table 2. Examples of greenhouse gas efflux from wetlands (not including coal or metal mine water wetlands) and notes on analytical methods employed

Reference	**Site**	**Wetland type**	**Measured gas flux**	**Field collection method**	**Gas analysis method**	**Other**
Teiter and Mander (2005)	3 sites in southern Estonia	Horizontal and vertical flow constructed wastewater treatment wetlands (planted with *Phragmites* and *Typha*). One riparian alder stand as natural reference.	Horizontal flow CW: N_2 = 0.17-130mgN_2-N$m^{-2}h^{-1}$; N_2O = 2.4-31µgN_2O-N$m^{-2}h^{-1}$; CH_4 = 30-9715µg CH_4-C $m^{-2}h^{-1}$; CO_2 = 61-140mg CO_2-C $m^{-2}h^{-1}$. Vertical flow CW: N_2 = 0.33-119mgN_2-N$m^{-2}h^{-1}$; N_2O = 35.6-44.7µgN_2O-N$m^{-2}h^{-1}$; CH_4 = -1.7-87200µg CH_4-C $m^{-2}h^{-1}$; CO_2 = 140-291mg CO_2-C $m^{-2}h^{-1}$	Closed chamber (closed soil cover box). He-O method via intact core analysis (for N_2)	GC (electron capture detector and flame ionization detector)	GWP of CW higher than that of natural wetland but global influence of CW for domestic wastewater treatment not considered significant.
Liikanen *et al.* (2006)	Kompsasuo, N. Finland.	Constructed minerotrophic wetland treating peat mining runoff. *Carex-Sphagnum.*	CH_4 = 5.8-16.7mg $CH_4m^{-2}h^{-1}$ CO_2 = 302.9-566.7 mg CO_2 $m^{-2}h^{-1}$. N_2O = 14.2-18.8µg$N_2Om^{-2}h^{-1}$	Static closed chamber. Gas samples taken with 50ml polypropylene syringes with 3-way stopcocks.	GC (HP P5890 Series II) equipped with flame ionization detector (for CH_4), electron capture detector (for N_2O) and thermal conductivity detector (for CO_2)	CH_4 production tripled over time and CO_2 doubled as plant biomass doubled during the course of CW operation.
Heinsch *et al.* (2004)	Nueces River Delta nr. Corpus Christi. TX, USA.	Variably saline estuarine marsh. Halophytic species.	CO_2 = 50-650mg CO_2 $m^{-2}h^{-1}$	Teflon tube and pumps separating updrafts and downdrafts feeding to gas analyser.	I-R gas analyser (Li-Cor LI-6262) in field.	-
Song *et al.* (2003)	Sanjiang Plain, China	Primary swamp – comparison of perennially inundated and seasonally inundated areas.	CO_2 = 548-713mg CO_2 $m^{-2}h^{-1}$ CH_4 =8.56-12.8 mg $CH_4m^{-2}h^{-1}$	-	-	CH_4 emission higher in area of perennial inundation. Respiration increases with soil and water temperature.
Stadmark and Leonardson (2005)	Ormastorp, Gorarp and Genarp, southern Sweden	Denitrification ponds with some aquatic macrophytes and floating aquatics.	CH_4 = <0.6-54 mg CH_4-C$m^{-2}h^{-1}$ CO_2 = no consistent pattern. Values not given	Closed static chamber. Gas samples taken with 10ml polypropylene syringes with 3-way stopcocks.	CO_2 measured in field using I-R gas analyser (EGM-4, PP Systems, UK). CH_4 measured in lab with Shimadzu GC 17A with flame ionization detector.	Water temperature +ve correlated with CH_4 production.