PESTICIDE SUSTAINABLE MANAGEMENT PRACTICE (SMP) INCLUDING POROUS BIOCHAR/GEOPOLYMER STRUCTURES FOR CONTAMINATED WATER REMEDIATION

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ABSTRACT: As a result of agribusiness in Australia and across the world, water is contaminated with nutrients and pesticides which threaten riverine environments, wetlands, urban drinking water supplies and also marine assets such as the Great Barrier Reef (GBR). Much can be done and sustainable management practices (SMP) can be put into place to reduce water impacts from agriculture. Required investment levels are insignificant compared to the economic advantages to be gained from adopting appropriate SMP across Australian and global agribusiness. SMP technologies need to be targeted at specific pesticides (eg. atrazine, simazine, diruron, ametryn, hexazinone, tebuthiuron, dieldrin, metalochlor, 2,4 D, triclopyr, picloram and bromacil). Surface runoff from agricultural enterprises is conventionally managed by retention lagoons facilitating water reuse on-farm, but these can be breached during heavy storms. Long term deep drainage from fields and seepage from lagoons can also lead to contaminated groundwater. Research, development and testing of appropriate non-leaking/reactive spillways and subsurface geostructures needs to take place across the various agricultural industries. For surface water it is suggested that spillways could be designed with replaceable biochar baffles, and for groundwater, trenches of biochar could form Permeable Reactive Barriers (PRB). The potential for green or brown waste material derived biochar products, which could be readily manufactured from farm refuse and manure, needs to be thoroughly investigated in this regard. The challenge for engineers is to come up with geostructural designs which are efficient, cost effective and which will be taken up and embraced by Australian and world agribusiness.

Keywords Sustainable, Pesticide, Herbicide, Contaminated Water, Biochar, Porous, Geopolymer, Enzyme

1. INTRODUCTION

The Great Barrier Reef (GBR) consists of 3000 coral reefs and over 1000 islands spanning 2300 km of coastline from Bundaberg to the tip of Cape York in Northern Queensland. The GBR is an important heritage listed ecosystem and is also a significant economic asset, which through tourism earns over Aus\$5 billion per year, But the GBR is now in serious environmental decline. In CSIRO's Scientific Consensus Statement published in 2013, it was stated clearly that the decline in the GBR was 'due to continuing poor water quality, cumulative impacts of climate change, and increasing intensity of extreme events'. The relative importance of these individual stressors, for example sea surface temperature, is largely unknown and is the subject of ongoing scientific research. Minimising carbon pollution to the atmosphere through effective taxation policy is obviously an important longer term priority, but there is also a more immediate requirement for agriculture, industry and urban communities to develop sustainable management practices (SMP) now, which minimise the contamination of rainfall runoff water, which flows directly the GBR.

From agricultural enterprises located within an adjacent catchment area of 424,000 km², priority pollutants are identified as suspended sediment (SS), nutrients (normally expressed as Total Nitrogen or TN), and pesticides (mainly photosynthesis inhibiting

or PSII herbicides). Fine sediments or clay (<50µm particle size) carry some nitrogen and phosphorus which chemically adheres to organic/clay components. Gully erosion from overgrazing can contribute significantly to this type of pollution. Other forms of nitrogen and most pesticides are dissolved in surface runoff water, and are carried to the reef though catchment drainage systems. Approximately 35 river systems contribute water to the GBR region. This paper covers in the main, the requirement for Australian agribusiness to address water pollution issues in the form of the last described category. One novel way in which this might be achieved is to deploy onfarm (or end of farm) practices and technologies which reduce or eliminate export of agricultural pollutants off farm. In a nutshell, this would take the form of specially designed dam and waste lagoon spillways, equipped with biochar structures. In the event of large flood events, the embedded biochar structures would be designed to absorb any PSII herbicide compounds present in the water.

Previously, agribusiness has attempted to reduce contamination of the environment with pesticides by implementing Integrated Pest Management (IPM) [1] which refers to a strategy which seeks to reduce reliance on synthetic chemical pesticides. It generally involves i) managing pests below economically damaging levels rather than seeking to eradicate them ii) relying on non-chemical measures, and, iii)

selecting and applying pesticides, when they have to be used, in a way that minimizes adverse effects on beneficial organisms, humans, and the environment. IPM involves integrating a range of tools and strategies for managing pests. These can be conveniently grouped in seven main objectives including i) using the correct spray equipment to produce the biologically optimum droplet size ii) optimising coverage iii) appropriate chemical selection, iv) preserving beneficial insects, v) preventing insecticide resistance vi) managing crop and weed hosts, vii) using trap crops effectively and viii) communication and training.

Field studies over the years have demonstrated that pesticide application using liquid based sprays is probably at best only a few percent efficient [2]. Efficiency is defined simply in terms of the percentage of droplets reaching the intended target. These studies have indicated that droplet size seems to be the most important factor which determines this efficiency. Droplets produced by conventional hydraulic nozzles used in agriculture generally range in size from 30um to 3000um. Droplets with diameters less than 100um have low sedimentation velocity and shallow trajectory, and are vulnerable to off target drift and loss to atmosphere. Droplets greater than 300um which contain most of the volume of the spray, have high sedimentation velocity and steep trajectory, and are unlikely to strike a plant surface or pest. Even within a dense crop canopy, coarse droplets may bounce from a leaves, and simply contribute to soil and/or therefore application pollution. Pesticide groundwater efficiency could be increased dramatically if the percentage of droplets falling between 100um and 300um present in the spray was increased [3].

Investment is also needed in developing appropriate remediation technology to pesticide contaminated water which leaves cultivated field as runoff. Green and brown waste derived biochar has recently shown significant potential in this regard. A particulate form of biochar is required to increase available surface area, with carbon particles held in a rigid and durable porous matrix, to prevent them being eroded away by a moving water stream. Recent developments in porous geopolymer concrete may perhaps provide an answer to this design challenge.

Such technologies when assembled together in a unified SMP strategy for sustainable agribusiness, will undoubtedly have the potential to significantly reduce pollution of atmosphere, soil, fresh water and oceans with pesticides.

2. PESTICIDE FATE AND BEHAVIOUR MONITORING AND MODELLING

Pesticides residues can be found in the atmosphere, water, soil, vegetation and organisms. In water, pesticides can exist in a dissolved form, or can

be attached suspended matter or bottom sediments. Pesticides are taken up by aquatic biota, possibly being excreted in metabolised form. Within a water system, transformation of pesticides can occur via chemical, physical and biological processes.

Pesticide runoff into natural water systems can occur during large rainfall or storm events. Weed control in urban areas is often adjacent to hard surfaces and roads with man-made drainage systems acting as a fast conduit to ocean. Correctly designed storm water harvesting infrastructure is often non-existent, or at best minimal. Farms are usually designed with retention storages whose combined purpose is to collect irrigation tail water and storm water runoff. However, during periods of high rainfall, on-farm storage of runoff can be breached, and pesticides are at risk of entering the river systems and making it out to the GBR [4].

The development of numerical models to describe pesticide fate and behaviour commenced in the 1970s and 80s, and were useful in understanding DDT found in birds of prey, in the wildlife at both poles, and also in dairy cattle directly affecting humans. Endosulfan was found in Australian export beef during the 1990s. HowLeaky? software [5] which was launched by Old Govt DNRM, DAFF and EPA in 2003 represents the pinnacle of development for pesticide fate and behaviour modelling purposes. Evolution of the software from exhaustive testing and calibration earlier algorithms (USLE, CREAMS, GLEAMS, RZWQM, HSPF, PRZM, PERFECT and WASP). The model represents a one dimensional soil/water balance agricultural hydrology model for exploring the impact of different land uses and soil management on water balance and water quality. It has a user interface which provides a highly visual representation of inputs and outputs. The software has been used to explore implications of different land uses (including crops, pasture and tress), climates, soil types and management (tillage, crop rotation, herbicide strategies) on hydrology, production index, erosion and off-site sediment loss, nitrogen, phosphorus and pesticide movement [6].

3. WATER REMEDIATION USING POROUS BIOCHAR GEOSTRUCTURES

The use of ground iron based reactive barriers for TCE to ethane, Cr(VI) to Cr(III), some heavy metals and phosphorus has been investigated by the USEPA, but focus is now on non-living structures for pesticide/nutrient bioremediation, because of the problem of keeping the plants/microbes alive is alleviated. The advantage of using biochar geostructures is longevity and reduced maintenance costs. Added to soil in particulate form, studies have demonstrated that biochar can increase cation exchange capacity, enhance soil microbes and augment water retention [7,8]. These advantages are

additional to its primary use as a soil carbon store for greenhouse gas reasons. It has also been suggested that biochar can reduce nutrient loadings in agricultural runoff. It is established that biochar on its own is showing promise also for the removal of some heavy metals [9] and uranium [10]. In trials in which particulate biochar was added to soil as a soil amendment, it was noticed that herbicide efficacy in controlling weeds was noticeable reduced [8].



Fig 1 Perspex box constructed at USQ, for purposes of visually demonstrating of the concept of a biochar filled trench ie. a Permeable Reactive Barrier (PRB) for shallow groundwater remediation. The simulated pollutant water entered at top left contains an organic fragrance plus blue food colour. It can be demonstrated that the blue food colour travels with the water straight through the biochar barrier, but the organic fragrance is arrested by the carbon.

The reason for this is presumably chemical binding of the herbicide active ingredient to the carbon particles. From this has very recently launched a series of investigations as to the potential effectiveness of biochar for removal of herbicides in water [11]. The potential for biochar derived from greenwaste has been assessed specifically for triazine based herbicides [12]. The potential for biochar derived from pig manure has been assessed for the herbicide paraquat by [13] and for carbaryl plus atrazine by [14]. Deep percolation of pesticides leads to long term pollution of groundwater resources and represents a new area which needs to be addressed. investigations **Preliminary** of biochar geostructures commenced at USQ [15] and Figure 1. Perspex boxes have been constructed for visually investigating the concept of a biochar filled vertical trenches ie. a Permeable Reactive Barrier (PRB) for shallow groundwater remediation. The simulated pollutant water entered at top left contains an organic fragrance (eg. vanilla essence) plus blue food colour. It can be demonstrated that the blue food colour travels with the water straight through the biochar barrier, but the organic fragrance is arrested by the carbon, as it is non-detectable at the end of its travel through the medium. Several designs have been produced, some with the layer of biochar arranged horizontally, and covered with a protective gravel layer.

4. DISCUSSION

It has been recently estimated that 12-17 tonnes of PSII herbicide active ingredient (a.i.) per year, on average, are exported to the GBR ecosystem. [17,18,19,20,21,22]. This corresponds very approximately, to one or two percent of the total PSII herbicide applied to the GBR catchment annually. However, in particularly wet years with large storm events, this figure may be substantially higher, leading to significant and catastrophic damage to the GBR ecosystem. Hydrological research is being conducted presently, to determine the maximum loading which may have happened in any one year.

The relative contribution of the various different types of herbicide importance of different types can further determined from available monitoring data, and calculated catchment loading figures. The most significant chemicals involved would be atrazine, diuron and ametryn, with estimates of around 600 tonnes (a.i.) of these chemicals per year being applied in Queensland sugarcane production alone [21]. Other PSII herbicides applied in lesser amounts include hexazinone, metribuzin and simazine. Non-PSII herbicides that are also detected in reef waters include tebuthiuron, dieldrin, metalochlor, 2,4-D, triclopyr, picloram and bromacil. Rainfall simulation studies over many years, and collated by [21] will assist greatly in the design of on-farm geostructures for agricultural water clean-up. As a rule of thumb, typically 1 mg/kg of PSII herbicide present in the upper 25cm of paddock soil, would normally produce a concentration in runoff of 10-50µg/L for most herbicides. Depending on cropping type, calculated PSII source strengths are typically 10-50g/ha/yr [22]. Armed with this very useful data, hydrologists and environmental engineers can calculate the likely loading and performance characteristics of any biochar based geostructures which they design.

One way in which engineers could significantly contribute to the important task of lessening the chemical loading to the GBR, is to construct hydraulic structures, which treat water on its way downstream, during large storm events. Existing dam spillways could be modified or new ones specially constructed. If spillways located downstream of farm enterprises were equipped with suitably designed biochar baffles, this might represent one practical SMP approach by which stream transport of agrochemicals could be significantly reduced during

major storm events. An appropriate engineering design might be similar to the spillway design at Yeoman Hey Reservoir, constructed in northern England in 1880. (Figure 2).



Fig. 2 Baffled spillway with concrete block baffles located at Yeoman Hey Reservoir, Saddleworth, UK. One concept presented in this paper would be to have biochar encased in heavy duty wire mesh boxes, forming anchored baffle elements, replaceable using light crane. Research needs to be carried out optimise geometrical specifications, in relation to performance versus economic considerations.

Biochar (or charcoal) would be manufactured as large (~200cm³) structurally competent pieces, and would be encased in heavy duty wire mesh boxes, forming the porous baffle elements (~1m³). These elements would be securely anchored into recesses places in the concrete spillway, and would be replaceable using light crane. Detailed research needs to be carried out to optimise the geometry of biochar baffle structures, in relation to performance versus economic considerations. Investigations need to take place to determine how long (ie. how many heavy rainfall events) the baffles would last for, and if their performance could be lengthened and improved using engineered enzymes.

5. CONCLUSION

SMP strategies to control pesticide pollution may take the form of improved spraying technology (eg. narrowing the droplet size distribution and band application), improved integrated pest management, improved timing of applications in relation to large storm events, and reduced tillage and stubble retention practices to reduce soil erosion. Scientists need to acquire a better understanding of herbicide environmental fate and behaviour, particularly persistence characteristics in soil and crop residues, and also sorption/desorption characteristics during instream transport.

There is now a strong requirement for hydrologists and environmental engineers to gain a better understanding surface and groundwater flow patterns, and develop SMPs and appropriate contaminated water remediation technologies. Work in collaboration with biochemists needs to take place to develop enzymes which are naturally found in pesticide resistant insects or weeds. Biochar geostructural/geopolymer based technologies need to be developed, augmented with enzyme based products which need to be developed commercially. Such products or enhancers need to be targeted at the specific herbicides detected in GBR waters.

Extensive deployment of and testing of several geostructural designs needs to take place, as deemed necessary and appropriate across the various agricultural industries. Surface runoff needs to be managed, with properly designed retention lagoons facilitating water reuse on-farm, featuring biochar baffle spillways for storm water management purposes. The potential for green or brown waste material derived biochar products, which could be readily manufactured from farm refuse and manure, needs to be thoroughly investigated in this regard. Loss of contaminated water via field deep drainage presents a much tougher problem which up until now has not been satisfactorily addressed. The challenge for engineers is to come up with both surface and sub-surface geostructural designs which are efficient, cost effective and which will be taken up and embraced by Australian and world agribusiness.

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