Bioavailability, causation and correlation: can we really conclude the herbicide diuron resulted in mangrove dieback in river estuaries of Central Queensland?

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Abstract
Statistically significant correlations in the form of dose-response relationships can provide valuable evidence to support the case that a particular stressor has caused an environmental impact. However, the selection of a parameter representing the dosage requires careful consideration if meaningful assessments of causation are to be made. Application of the concept of bioavailability can provide a valuable tool for parameter selection. This approach is applied to the proposition that the herbicide diuron is implicated in mangrove dieback in river estuaries of Central Queensland.

Key Words
Bioavailability, Correlation, Causation, Herbicide, Sediment, Mangrove.

Introduction

Runoff of agricultural chemicals in catchment areas adjacent to the Great Barrier Reef (GBR), particularly pesticides (Lewis *et al*. 2009) and nutrients (O'Reagain *et al*. 2005) has been a major concern over the past decade. These contaminants have been associated with detrimental impacts on various organisms, particularly mangroves (Duke *et al*. 2003, 2005), seagrass (Haynes *et al*. 2000) and coral (Jones *et al*. 2003). Herbicide residues have been detected in waterways of the GBR catchment area (Mitchell *et al*. 2005) as well as in intertidal and subtidal sediments (Haynes *et al*. 2000). However, it is wrong to conclude that the mere presence of a chemical in the environment causes harmful biological impacts to organisms. This paper demonstrates the importance of considering basic knowledge of bioavailability to avoid erroneous conclusions regarding causation.

Causation and correlation

Causation does not necessarily follow from a correlation between an observed biological impact and the presence of a particular stressor in the environment (Beyers 1998). Nevertheless, correlations are often useful indicators of causation, particularly when used in combination with other criteria (Adams 2003). Where chemical stressors are implicated, the correlations examined will usually take the form of a dose-response relationship. This in turn requires careful consideration of the concept of bioavailability.

Bioavailability, and selecting an appropriate dose parameter

A generalised representation of bioavailability processes in a soil or sediment is shown in Figure 1. This can be applied to the case where the putative environmental stressor is an organic contaminant (X). Process A represents partition of X between solid soil/sediment surfaces and its dissolution in the aqueous phase. Process B represents direct uptake of the sorbed X by the organism from the solid, whereas process C represents direct uptake of dissolved X from solution. Bioavailability of X will depend on the organism, and the appropriate dose parameter will depend on whether process B, or C or a combination of B and C are important. This is illustrated by considering uptake of X by three different organisms – (i) soil microbes; (ii) earthworms; and (iii) plants, in the context of processes illustrated in Figure 1.

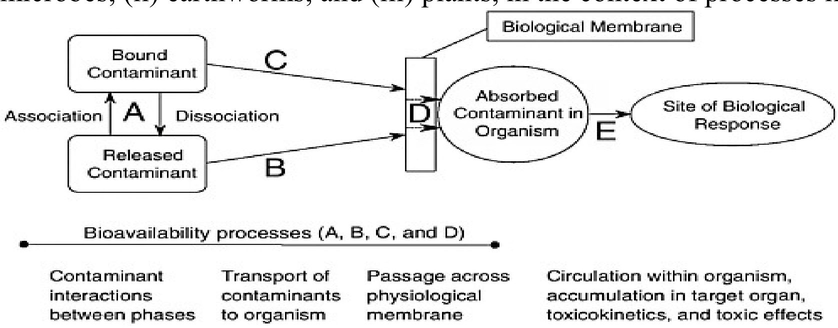

Figure 1. Bioavailability processes in soil or sediment. (Committee on Bioavailability (2003). Note – 'Bound Contaminant' in this reproduced figure is equivalent to "sorbed contaminant' as discussed in the text.

Soil-sorbed organic contaminants are generally considered unavailable for microbial biodegradation without prior desorption (Ogram *et al*. 1985; Yang *et al*. 2006). However, evidence suggests that some soil-sorbed contaminants can be degraded by specific microorganisms or at least that desorption into bulk solution is not a prerequisite for biodegradation (Guerin *et al*. 1992; Tang *et al*. 1998). Consequently, for microbes, process C is generally dominant for uptake of X, but process B can also be important in exceptional cases.

A distinction can be made between "bioavailability" and "bioaccessibility" (Semple *et al*. 2004). Bioavailability is defined as material freely available to cross an organsm's cellar membrane from the medium an organism inhabits at a given time. Where a constraint is imposed in time/space, the material may be considered bioaccessible but not bioavailable.

Only the chemical dissolved in the soil solution is thought to be environmentally bioavailable to the earthworm for dermal uptake (Belfroid *et al*. 1996). However, earthworms can also ingest soil with X sorbed on solid surfaces, subsequently subjected to the chemical conditions present in the animal's gastrointestinal tract (Lanno *et al*. 2004). Therefore both processes B and C will generally be important for earthworms.

For plants, it has long been established that the bioavailability of organic chemicals associated with soils and sediments, including many common herbicides, depends primarily on the uptake of the dissolved organic molecule in the aqueous phase in the root zone (Pillay and Tchan 1971; Boesten 1993). This has been demonstrated for uptake of simazine by oat and cotton seedlings (Sheets 1961), uptake of atrazine by wheat plants (Walker 1972), and for carrot, parsnip, lettuce, and turnip seedlings (Walker and Featherstone 1973), and more recently for accumulation of atrazine within the shoots of rice seedlings (Su *et al*. 2007). Consideration of bioavailability therefore shows process C, but not process B, will be important for uptake of X by the root system of a plant. This, in turn, tells us that the concentration of X in solution, not the concentration of X sorbed on solid surfaces of a soil or sediment should be used to represent the dose parameter.

A case study – diuron and mangrove dieback

Mangrove dieback has been reported in the river estuaries of Central Queensland, following major flooding events in 1998 in the Pioneer River and 2008 in the Fitzroy River, mainly affecting the species *Avicennia marina*. These events were widely reported in the media, with some researchers suggesting that the cause of the dieback was related to the herbicide diuron, used in production of sugar cane. However, when dose-response relationships are examined, as illustrated in Figures 2A and 2B, there is no statistically significant correlation. Using this dose parameter, based on consideration of bioavailability, there are no correlations to support the claim that diuron has caused the dieback. Furthermore, it is interesting that Wake's data deals with much higher concentrations of diuron reporting 100% healthy trees at 60 ng/litre diuron, but Duke's maximum concentration is less than 15 ng/litre. This finding is in contrast to the conclusions previously drawn where bioavailability was not considered, and only process B was considered relevant (Duke *et al*. 2003). This is illustrated in Figure 3 where the dose parameter applied was the concentration of diuron sorbed on the sediment.

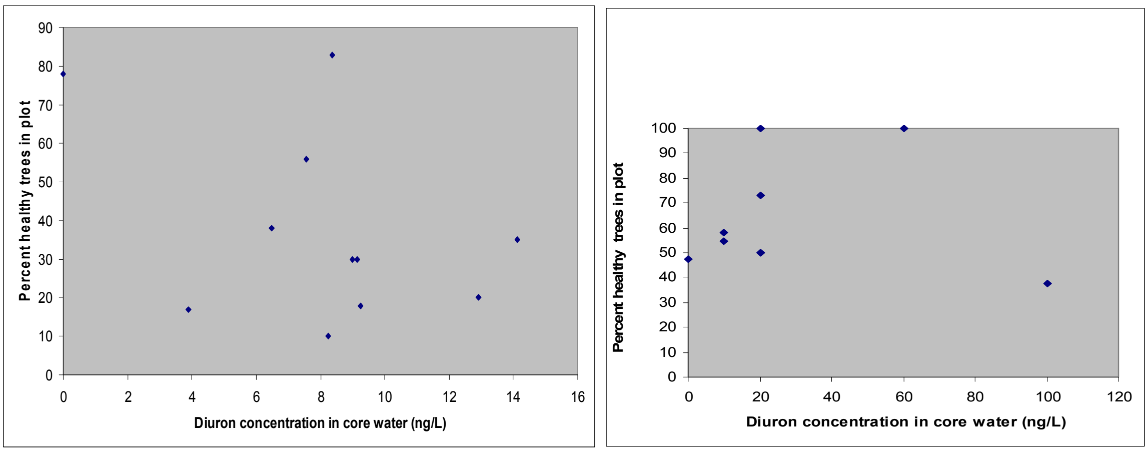

Figure 2. Percentage of healthy mangroves plotted against concentration of diuron in root zone core water at sites in CQ river estuaries. A: in 2002 (Duke *et al.* 2003) (r = -0.401); B: in 2004 (Wake 2005) (r = 0.025).

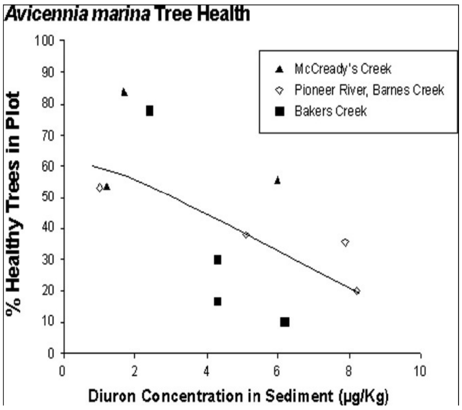

Figure 3. Percentage of healthy mangroves plotted against concentration of diuron sorbed on sediments at sites in Central Queensland river estuaries in 2002. Reproduced from Duke (2008) (r = -0.6544).

The correlation reported by Duke (Duke *et al*. 2003, 2008; McKillup 2008) is not useful for establishing causation. The dose parameter does not take account of the dominant process whereby diuron uptake occurs via the mangrove roots. There is no evidence in the literature that mangroves can directly uptake sorbed diuron, as in the case of microbes (Guerin *et al*. 1992; Tang *et al*. 1998), nor ingest sediments as in the case of earthworms (Lanno *et al*. 2004). Moreover, it is important to understand that there is no direct proportionality between diuron concentration in root zone solution and herbicide sorbed on sediments where samples from different locations are considered, as in Figure 3. Differences in sediment organic content, (Walker 1972) mineral composition (Gilchrist 1993) and moisture content (Lambert 1966) at different locations are well documented for mangrove sediments (Duke *et al*. 2003; Wake 2005) and rule out any simple concentration proportionality.

Conclusion

A consideration of bioavailability is important before selecting a relevant dosage concentration parameter if the objective is to examine correlations for dose-response relationships in order to support or refute evidence for causation. For the case study presented, application of this principle shows that causation of mangrove dieback by Diuron in the river estuaries of Central Queensland is not supported.

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