

NUCLEAR AND ISOTOPIC TECHNIQUES UNDERPINNING PROBABILISTIC ECOLOGICAL RISK ANALYSIS IN COASTAL MARINE SYSTEMS

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1. Introduction

The historical operation of manufacturing, chemical and other industries in the Sydney Harbour catchment over many decades has resulted in a legacy of high chemical contamination, such that a recent report describes Port Jackson as one of the most contaminated harbours in the world [1]. The contaminant legacy in Homebush Bay is one of the worst in the harbour and presents a considerable management problem. Consultation with environmental managers (NSW Department of Environmental Conservation, NSW Fisheries, Sydney Olympic Park Authority) have identified that the presence of contaminated estuarine sediments present a complicated management issue in several coastal situations in NSW, including Homebush Bay (Figure 1). Although environmental managers are beginning to understand that elucidation of environmental processes is the key to effective ecosystem management, few tools are presently available to determine the in situ inter-relationships, rates and pathways of these events.

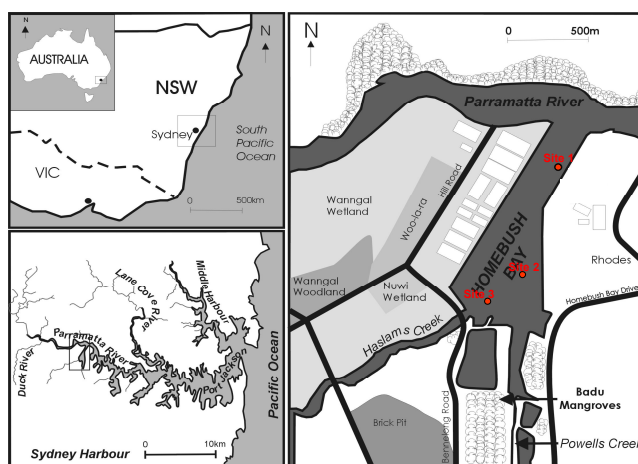


Figure 1. Locality map for studies in Homebush Bay, NSW.

Understanding the ecological risk imposed by contaminants in estuarine sediments requires an understanding of (1) specific trophic linkages and keystone species, (2) incident contaminant levels and, for predictions, the frequency/duration of physico-chemical processes (resuspension, desorption and transport), and (3) biological uptake/transfer mechanisms under a range of incident environmental conditions.

Nuclear & isotopic techniques have a wide utility in coastal zone process studies with distinct advantages over conventional methods. Highly accurate and specific information on ecological, physical, chemical and biological processes may be obtained by selection of proxy isotopes with the appropriate properties. Nuclear tracers may be naturally occurring isotopes characteristic of the particular process under investigation, artificial and introduced as analogues of natural products, or labels on substances retrieved from nature. Here we will apply a range of nuclear and isotopic techniques to study the behaviour of metal contaminants associated with the sediments of Homebush Bay and their passage through the local food-web (Figure 2).

This study has four main activities: (1) Determination of the linkages between high trophic order species and different habitat resources using $\delta^{15}\text{N}$ & $\delta^{13}\text{C}$. These studies identify trophic cascades (food chains) which form the basis for selection of biota for contaminant transfer experiments. (2) A short-term (weeks – months) chronology of the surface mixed-layer of sediment cores collected from Homebush Bay will determine the rate of sedimentation and resuspension (using environmental/cosmogenic 7-beryllium). Models derived from these studies provide the levels of contaminants against which risk is assessed. (3)

Biokinetic studies using proxy radiotracer isotopes (eg. artificial ^{75}Se & ^{109}Cd for stable metals) of the uptake and trophic transfer of selected contaminants by specific estuarine biota. Here we identify the rates and extent to which contaminants are accumulated and transferred to predators/seafoods. (4) Application of an environmental risk assessment model (AQUARISK) set to criteria determined by stakeholder consensus.

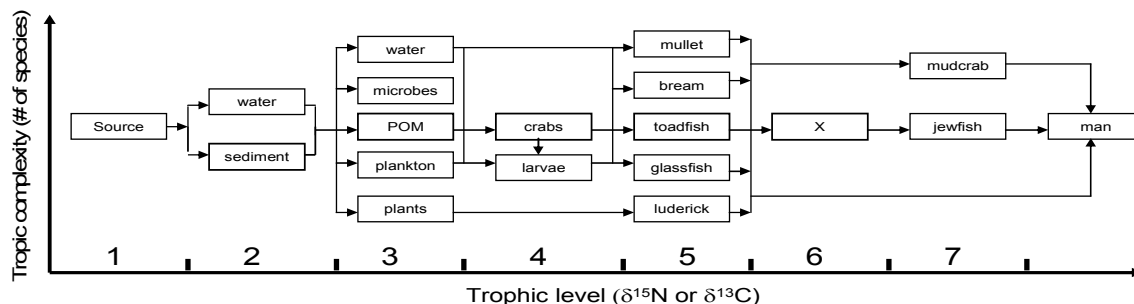


Figure 2. Postulated trophic food web for a local estuary and pathways for transfer of contaminants to man.

2. Tracing trophic linkages in aquatic food webs using stable isotopes

In recent decades there has been a rapid expansion in the use of stable and radioactive isotopes in many areas of environmental research. It is important, however, to appreciate that stable isotope applications are most effective when used in combination with other techniques that enable the quantification of processes (eg. radiotracers, which maybe naturally occurring) and analysis of contaminants in water, sediments and biota. Isotopic studies become powerful tools for tracing the flow of contaminants through catchments and food webs, and for understanding the relationships between trophic (food web) levels and bioaccumulation.

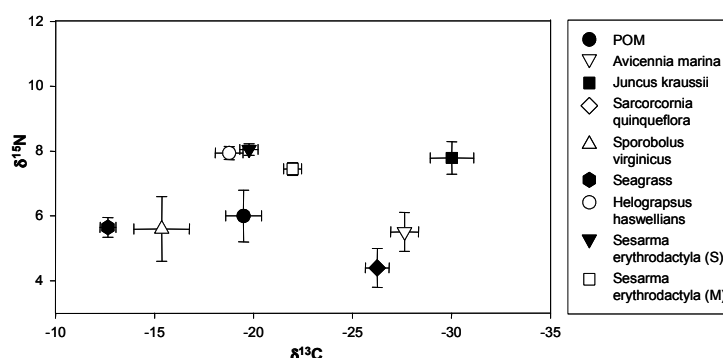


Figure 3. $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ ratios of producers and consumers at Towra Point, NSW, modified from [2].

Ecological applications of stable isotope analysis rely on producer distinct isotope ratios of carbon and nitrogen which are transferred to consumers. Metabolic processes result in fractionation and enrichment of the isotopic ratios (i.e. they become higher) in both carbon and nitrogen compared to the diet. In this way, we are able to determine at what trophic level an animal is feeding in relation to its ecosystem.

Carbon and nitrogen isotopes were used to study trophic linkages between burrowing crabs and primary producers in saltmarsh [2, 3]. The results suggested different species of crabs living in the saltmarsh (*S. erythrodractyla* and *H. haswellianus*) were reliant on the same food source for their nutrition, ie, particulate organic matter (POM) rather than the presumed incident saltmarsh and mangrove plants (Figure 3).

3. Quantifying contaminated sediment dynamics using shorted-lived radioisotopes

An understanding of the complex interaction of processes occurring in sediments (deposition, diagenesis, resuspension, transport) is essential for determining contaminant availability. Hydrophobic contaminants associate with suspended particles and colloids and deposit in estuaries and embayments. While many of the contaminants are strongly bound to the particles, or may release very slowly, others are released quickly into the water column through changes in geochemistry via diagenesis, bioturbation or resuspension.

The distinction in time scales between temporary and permanent storage of sediments/particulates in estuaries is important in determining the ultimate fate of pollutants. Naturally occurring radioisotopes can be used to quantify these differences in time scales, by establishing the geochronology of the bottom sediments. They can also be used to determine rates of sedimentary processes and fluxes of sediments. The most commonly used sediment particle tracers are naturally occurring radioisotopes such as ^7Be , ^{234}Th and ^{210}Pb .

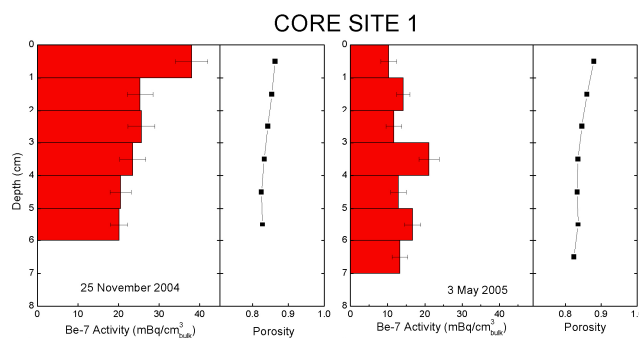


Figure 4. Vertical profiles of ^7Be in sediments from Homebush Bay, NSW.

Deposition is the temporary emplacement of sediment on the estuary bed and can be measured using ^7Be (Figure 4) and ^{234}Th because of their short half-lives (53.3 days and 24.1 days respectively). On the longer time scale of years to decades, sediment accumulation can be determined by using ^{210}Pb (half-life of 22.3 years) or ^{137}Cs (half-life of 30.2 years). By comparing deposition to accumulation rates, it is possible to determine the net export of sediment from an area or the short-term resuspension rates. This approach is currently being applied in Homebush Bay, Sydney in a study to determine the fate of sediments, heavy metals and other pollutants.

4. Biokinetic studies of uptake and trophic transfer of contaminants by estuarine biota.

4.1 Dietary uptake and depuration of ^{75}Se & ^{109}Cd by smooth toadfish (*Tetractenos glaber*)

Metals can be accumulated by biota from the water column, sediment or diet, and further bioaccumulate through the food chain and eventually impact on human health [5]. However, little is known about accumulation or regulation of metals in fishes, particularly marine and estuarine fishes. Uptake pathways in fish may include exposure through diet (benthic prey items living among contaminated sediments), water (direct exposure of metals via the gills) and sediments (ingestion of sediments). Metals in contaminated sediments may persist and impact upon estuaries for decades. Although water quality is slowly improving in Sydney estuaries, aquatic organisms continue to accumulate persistent metal contaminants [6].

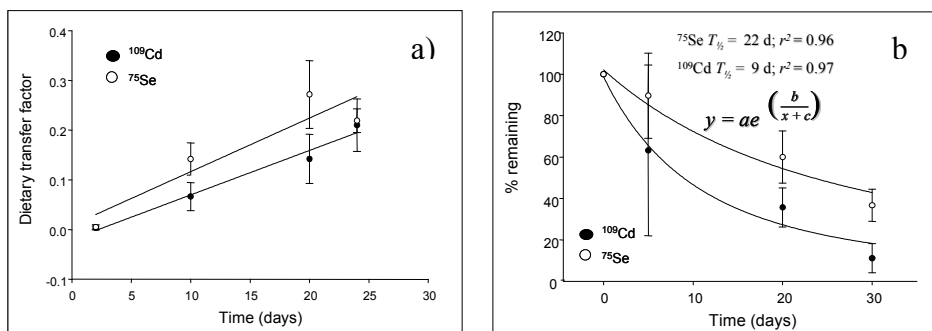


Figure 5. (a) ^{75}Se and ^{109}Cd dietary transfer factors for *T. glaber* from *Calinassa* sp. (mean $\pm$ SE), and (b) depuration (%) of ^{75}Se and ^{109}Cd by *T. glaber* (mean $\pm$ SE) [7].

The smooth toadfish (*Tetractenos glaber*) is a common, site-specific fish that preys on resident benthic infauna and often burrows in the sediment. The experimental aims of this study were (1) to investigate metal

uptake via dietary exposure and depuration in smooth toadfish using radioisotopes of ^{109}Cd & ^{75}Se and (2) to determine kinetics of metal transfers in organs of toadfish [7].

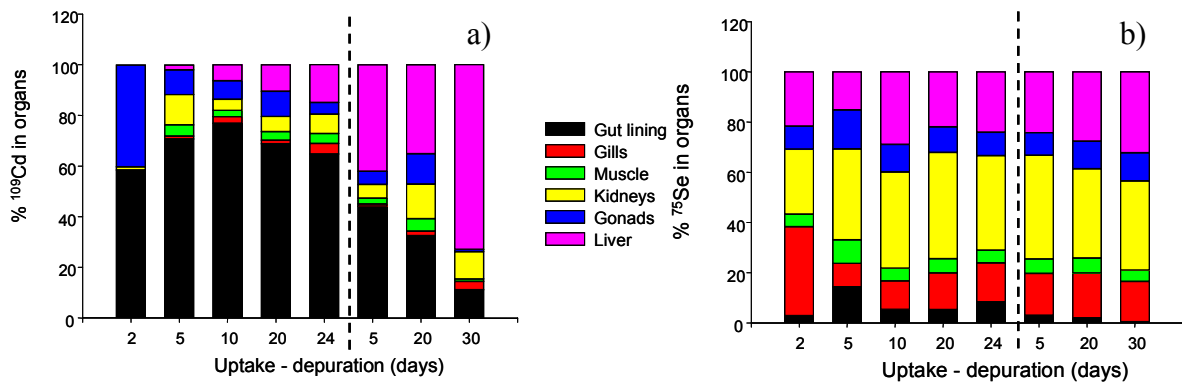


Figure 6. (a) ^{109}Cd and (b) ^{75}Se distributions in organs of *T. glaber* [7].

Results demonstrated that toadfish took up ^{75}Se at a slightly higher rate than ^{109}Cd (Figure 5a) but ^{75}Se was depurated in toadfish at a slower rate than ^{109}Cd (Figure 5b). Gut lining was the main target organ for ^{109}Cd uptake in toadfish and later transported to the liver for metal regulation (Figure 6a). Toadfish were able to depurate/excrete ^{75}Se throughout the experiment by sending metals to liver, gills and kidneys (Figure 6b).

4.2 Uptake of cadmium and selenium by the marine macroalga (*Ulva lactuca*)

The macroalgal genus *Ulva* was chosen for study because it has an ideal size and structure for laboratory experiments, is common in the local coastal area, and is an important component of coastal food chains [8]. A single *Ulva* species may exist in many morphological forms during the year, which has lead to multiple identifications of the same species [8], therefore all plants were collected from the same site to minimise species variability. Here we aimed to investigate not only the individual effects of differing levels of the macronutrients nitrate and phosphate on metal uptake, but also the combined effects of the two nutrients.

	Nitrate	Phosphate	Nitrate*Phosphate
Biomass	Did not change	Did not change	Did not change
Cadmium concentration	Increased**	Did not change	Decreased*
Selenium concentration	Did not change	Decreased*	Increased**
Photosynthetic efficiency	Increased**	Did not change	Did not change

Table 1: Effect of nutrients on uptake of ^{75}Se & ^{109}Cd by *Ulva lactuca* (* = $p < 0.05$, ** = $p < 0.01$) [9].

Results indicated that cadmium uptake by *Ulva* was linear ($R^2=0.9851$) [9]. Selenium uptake maybe described as either linear ($R^2=0.8889$) or first-order ($R^2=0.9049$). Increased nitrate concentration in solution influenced the accumulation of cadmium by *Ulva*, but did not affect selenium uptake (Table 1). Phosphate concentration in solution did not affect the accumulation of cadmium by *Ulva*, but reduced selenium uptake. Nitrate and phosphate interacted with each other, increasing the uptake of selenium but decreasing cadmium uptake by *Ulva*. Cadmium and selenium decreased the growth rate and photosynthetic efficiency of *Ulva*.

5. Combination and integration of environmental models

Environmental managers are beginning to understand that elucidation of environmental processes is the key to effective ecosystem management, however due to the complexity of coastal environments few tools are presently available to truly determine the inter-relationships, rates and directions of these events. It is only when all of these variables are understood and computationally described that effective ecological risk assessment can be accomplished. Many model packages already exist which describe and predict specific environmental processes and although further refinement of subroutines and user-interfaces has some value, the truly significant advances to be undertaken lie in the synergistic integration of different modelling codes.

Predictive ecological risk assessment requires bioaccumulation and trophic transfer models using keystone species (or critical groups) identified by models elucidating trophic structure and specific prey-predator associations. These in turn need to be driven by the output from contaminant transport models producing the source terms, or incident contaminant concentrations under a range of environmental conditions.

Integrated modelling is now needed more than ever in order to solve the most vexing of scientific and societal problems, e.g. the impact of human perturbations and/or climate change on water resources and ecological systems. The integration of new probes and tools and establishment of unconventional research teams introducing sociologists and resource economists to ecological systems analysts precludes the pathway to effective management.

6. Probabilistic ecological risk assessment modelling

Over the past decade, several studies have characterised the concentrations and distributions of metals in Sydney Harbour sediments [1]. However, to make this information of use to stakeholders and allow for appropriate environmental management decisions, the implications of those metal concentrations on ecosystem and human health need to be evaluated by a scientifically defensible risk assessment approach.

Probabilistic ecological risk analysis (ERA) is a means whereby the risk posed by a toxicant in any system can be evaluated by comparing the distribution of its measured or modelled concentrations (water quality data - WQD) with available information on the range of concentrations that are known to adversely affect biota within that, or similar, habitats (dose-response data - DRD). Initially, the WQD are compared with regulatory criteria (e.g. ANZECC/ARMCANZ, 2000). If they fail this test, then, on the assumption that both data sets comprise subsets of the entire range of concentrations, probability density functions are derived assuming a standard distribution form – typically log-normal. The WQD and DRD distributions are then convoluted to estimate (a) the likelihood that WQD will exceed set criteria derived from the DRD, and (b) the proportion of taxa likely to be affected. The criteria derived from the DRD usually comprise an estimate of the concentration that is hazardous (HC) to a set proportion of taxa (e.g. HC₅ for 5% of taxa) and an estimate of the uncertainty (e.g. HC_{5;95} would be the 95% lower uncertainty value of the HC₅) [12].

The AQUARISK code [10] has been developed to derive these criteria and estimate the risk of their exceedence. In addition, the geochemical speciation code MODPHRQ [11] included in AQUARISK evaluates the bioavailable fraction (ie the concentrations of those metal species present that are able to cross biological membranes) for copper and other metals in water. The speciation modelling is designed to overestimate the actual bioavailable concentration when any of the influential parameters are unknown. AQUARISK also estimates the average concentration that should be achieved to satisfy the regulatory, or DRD derived criteria, with an agreed exceedence, or that is likely to be tolerated by a set proportion of taxa. An initial risk map for Sydney Harbour (or more specifically on Homebush Bay as a test case), based on stakeholder agreed acceptability criteria, will be generated using simplified hazard exposure pathway models and literature-derived dose-response criteria relevant to the desired outcomes.

7. Technology transfer to developing countries via IAEA/RCA

The IAEA/Regional Cooperative Agreement (RCA) Project *Improving Regional Capacity for Assessment, Planning and Responding to Aquatic Environmental Emergencies* (RAS/8/095) is providing training and demonstration activities focused on improving the capacity for the management of aquatic radiological and environmental risks within the RCA Member States. The Project objectives are to improve the regional capacity for the management of aquatic radiological and environmental risks and to develop capacity in the RCA countries to assess, plan, and respond to such pollution in aquatic environments. Ecological risk analyses of the impact of contaminants on aquatic environments in Thailand and Indonesia using a range of nuclear, isotopic and modeling techniques are established as demonstration and training studies. Expert missions support national projects in individual Member States, further developing and transferring skills and technologies. A framework for acquisition of local information has been developed to gather data on sources of contaminants in the region and distribution of contaminants by National Project Teams. These

data contribute to a regional database, ASPAMARD [12], initiated under a previous RCA project on *Managing the Marine Coastal Environment and its Pollution* (RAS/8/080) [12].

8. Conclusion

In an attempt to elucidate natural processes, or solve environmental problems stable and radioisotope tracers have a number of advantages over conventional techniques. Stable isotope studies replace visual observations of prey-predator interactions with statistically interpretable chemical data. Radiotracer techniques can provide real time kinetic data on uptake and transfer of specific contaminants and environmental transport processes. The unique assemblage and application of these nuclear and isotopic environmental probes will greatly assist in effective ecological risk assessment of present situations and the resource-economic evaluation of proposed management options. The results and strategies developed from studies undertaken in the Sydney environs are directly transferable to other locations in NSW and elsewhere in the Asia-Pacific region - further sites are being considered via consultation with stakeholders.

9. Acknowledgements

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