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Spatial and temporal variability in particle-bound pesticide exposure and their effects on benthic community structure in a temporarily open estuary

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A B S T R A C T

Spatial and temporal variations in particle-bound pesticide contamination, natural environmental variables, and benthic abundance were measured during the dry summer season within a temporarily open estuary (Lourens River). This study focused on the effect of particle-associated pesticides on the dynamics of the benthic community (including epi-benthic, hyper-benthic, and demersal organisms) by comparing two runoff events, differing in their change in pesticide concentration and environmental variables. The two chosen sites were situated within the upper and middle reaches of the estuary and differ significantly in salinity ($p = 0.001$), flow ($p = 0.5$), temperature ($p < 0.001$) and particulate organic carbon in the sediment ($p < 0.001$). Generally higher particle-bound pesticides were found in the upper reaches.

The first runoff event was characterised by an increase in pesticides (chlorpyrifos, endosulfan and cypermethrin) and hardly any change in natural environmental variables, whereas the second runoff event was characterised by no increase in pesticide but a significant change in natural environmental variables like salinity, temperature and flow. The most evident spatial difference in community structure was shown by the use of Principal Response Curve after the first runoff event, whereas no response was shown after the second runoff event. The variables which explained most of the spatial differences are Total Organic Carbon, salinity, chlorpyrifos and endosulfan concentrations. The species contributing most to the spatial differences are the estuarine harpacticoid *Mesochra* and *Canthocamptus* (lower abundance at the upper reaches) and the freshwater species *Dunhevedia* and *Thermocyclops* (higher abundance within upper reaches). Within the spatial variability (between upper and middle reaches) the authors were able to detect a link between endosulfan, chlorpyrifos exposure, TOC and salinity and community change by comparing the two runoff events.

1. Introduction

Temporarily open estuaries (TOE) are periodically closed off to the sea due to the lack of freshwater input. They show significant natural spatial and temporal variability in physical and chemical conditions (such as flow, salinity, temperature or total suspended solids). This variability is likely to be reflected in changes in community structures (Kibirige and Perissinotto, 2003). Trying to isolate fingerprints of contaminant effects is thus particularly difficult when their distribution is confounded with physical and chemical gradients. Methods of community description used to determine which variables and which taxa contribute to spatial and temporal differences between sites include: (a) community indices (e.g. species richness and Shannon Diversity Index) and (b) a multivariate approach, namely the Principal Response Curve. The Principal Response Curve (PRC) approach has been shown to be valuable in statistically analyzing multiple endpoints (Den Besten and van den Brink, 2005). The statistical methodology has already been used for bio-monitoring by other authors (Van den Brink and Ter Braak, 1999; Van den Brink et al., in press).

The study area in this investigation is the Lourens River estuary (Western Cape, South Africa). Previous studies (Bollmohr and Schulz, in press; Schulz et al., 2001) have shown that pesticides are the major contributors to pollution and associated effects in the

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Lourens River. Particles entering the estuary have been shown to be associated with high concentrations of chlorpyrifos (19.6 μg kg^{-1}), endosulfan (18.6 μg kg^{-1}) and prothiofos (34.0 μg kg^{-1}) (Bollmohr et al., 2007), with highest concentrations during the spring and summer seasons. The accumulation of these particles is enhanced by a number of factors and may show a spatial gradient in concentrations and effects during this season. These factors include the change from fresh to saltwater, the rise and fall of water level with the tides, the decrease in flow within the middle reaches of the estuary, and the influx of seawater.

This study has focused on community changes of organisms living in the flocculent layer between sediment and water column, including epi-benthic, hyper-benthic and demersal meiobenthos and zooplankton organisms. The advantages of using meiobenthos in contaminant assessment studies include their high abundance and species diversity, short generation time, fast turnover rates, ubiquitous distribution, and moderate-to-high sensitivity to contaminants (Kennedy and Jacoby, 1999).

More than 98% of all meiobenthic copepods live in the upper 1–2 cm oxic zone of muddy sediments (flocculent layer) and may thus be particularly affected by exposure to particle-bound pesticides (Chandler et al., 1997). Deposit- and suspension-feeding infauna living in contaminated sediments actively ingest potentially toxic food particles and circulate contaminated water. As a result, bio-concentration of insecticides in meiobenthos and other epi-benthic and hyper-benthic organisms can cause significant ecotoxicological effects, even at relatively low aquatic concentrations (Chandler et al., 1997). Copepods and meiobenthos as a whole are underrepresented in pollution studies (Coull and Chandler, 1992), yet they play a major role in estuarine carbon cycling and food webs. Their variability (daily and seasonal) can, however, be very high and difficult to correlate with environmental factors because of multifactorial relationships.

Many studies of meiobenthic community structure focus on the natural distribution and its driving variables like sediment composition (Sherman and Coull, 1980), salinity (Miliou, 1993) and food source (e.g. Decho and Castenholz, 1986). To determine the effect of pesticides on meiobenthos abundances, various studies have been performed using sediment toxicity tests (e.g. Chandler and Green, 2001; Bollmohr et al., in press) or microcosms (Chandler et al., 1997), but only a few studies using bio-monitoring in the field (Warwick et al., 1990) have been performed. Other studies have focused on seasonal fluctuations of meiofauna and zooplankton in South African estuaries in relation to the distribution of physical factors (Dye, 1983; Nozais et al., 2005), state of the estuary mouth (Kibirige and Perissinotto, 2003) and food web interactions (Perissinotto et al., 2000), but the current study is the first to include investigation of the effects of pollutants.

The objectives of this study are: (a) to examine the spatial and temporal variability in physico-chemical parameters, particle-bound pesticide concentrations and meiobenthic abundance during the dry season; and (b) to study the effects of particle-bound pesticides on the dynamics of the meiobenthos community by comparing two runoff events, differing in their change in pesticide concentration and environmental variables.

2. Materials and methods

2.1. Study area

The Lourens River estuary is a typical temporarily open–closed estuary (Whitfield, 1995). It is located in the Western Cape of South Africa, which has a Mediterranean climate and is characterised by high rainfall in winter and a dry summer. The estuary enters into False Bay, an approximately 40 km wide bay south-east of Cape Town. The Lourens River mouth is situated at S34°06′ and E18°49′ and the total river length is approximately 20 km. The entire estuary has a volume of approximately 0.710 km^3 and is characterised by a narrow outflow channel, a wide slow flowing middle reach and a narrow fast flowing upper reach. The study sites were situated in the middle reaches (lower site) and the upper reaches (upper site) of the estuary. A large section of the upper catchment comprises privately owned agricultural land with vineyards and apple, pear and plum orchards. The lower reaches of the total catchment area of 92 km^2 consist of residential and light industrial.

2.2. Pesticide application and seasonal weather data

The four-month investigation period (28 November 2002–28 March 2003) lays within the dry summer season with infrequent rainfalls (Fig. 1). The following pesticides (with corresponding loads) are applied to pears, plums and apples between August and February before fruit harvest (Dabrowski et al., 2002): organophosphates such as chlorpyrifos (686 kg ha^{-1}) and prothiofos (87 kg ha^{-1}); organochlorines such as endosulfan (158 kg ha^{-1}); pyrethroids such as cypermethrin (8 kg ha^{-1}) and fenvalerate (5 kg ha^{-1}).

There is a particularly high frequency of pesticide application during the summer season from November to January – the "high-spraying season" (Schulz, 2001). Only rainfall events above 10 mm are assumed to contribute to runoff with possible input of particle-bound pesticides (Schulz, 2001). Only two such events were recorded (Fig. 1). The first rainfall event on the 15th January (11 mm) occurred during the high-spraying season. The second, much heavier rainfall event on the 23rd March (30.2 mm) took place in the low-spraying season.

2.3. Physico-chemical measurements

Various physico-chemical parameters were measured during each sampling event. The flow was measured every meter across the cross-section of the estuary at the different sites using a flow meter (Hoentzsch Co, Waiblingen, Germany). Dissolved oxygen, pH, temperature and conductivity were measured with electronic meters from Wissenschaftliche Technische Werkstaetten GmbH, Weilheim, Germany. The salinity measurement was obtained by converting the conductivity values into salinity using an automatic converter (Fofonoff and Millard, 1983). Total Suspended Solids (TSS) were measured with a turbidity meter (Dr. Lange, Duesseldorf, Germany) and nutrients were detected by photometric test kits from Macherey & Nagel, Dueren, Germany. The total organic carbon (TOC) was measured using a quantitative method which is based upon the indiscriminate removal of all organic matter followed by gravimetric determination of sample weight loss (ASTM, 2000). Four sediment samples (top 15 cm) per site (within a 1 m^2 transect) were collected and analysed.

2.4. Pesticide analysis

Samples of insecticides (one sample per sample event) associated with suspended particles were accumulated continuously over 14-day periods by a suspended-particle sampler (Liess et al., 1996), from which they were sampled for analysis. The suspended-particle sampler consisted of a plastic container (500 ml) with a screw-on lid. A hole (2 cm in diameter) was cut into the lid. An open glass jar that was stored directly under the hole in the lid. The samplers were stored approximately 5 cm above the river bed by being attached to a metal stake which was fixed into the sediment.

Samples of suspended particles were extracted twice with methanol, and the methanol-soluble fraction was concentrated using C18 columns. Insecticides were eluted with hexane and