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Transport of NOX emissions from sugarcane fertilisation into the Great Barrier Reef Lagoon

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Abstract

The Great Barrier Reef World Heritage Area contains highly sensitive ecosystems that are threatened by the effects of anthropogenic activity including eutrophication. The nearby sugarcane plantations of tropical north Queensland are fertilised annually and there has been ongoing concern about the magnitude of the loss of applied nitrogen to the environment. Previous studies have considered the potential of rainwater run-off to deposit reactive nitrogen species into rivers and ultimately into the Great Barrier Reef Lagoon, but have neglected the possibility of transport via the atmosphere. This paper reports the results of a modelling study commissioned by Australia's National Heritage Trust aimed at assessing whether or not atmospheric deposition of reactive nitrogen from Queensland's sugarcane plantations posed a potential threat to the Great Barrier Reef Lagoon. Atmospheric dispersion modelling was undertaken using The Air Pollution Model, developed by Australia's Commonwealth Scientific and Industrial Research Organisation. Despite the predominance of onshore southeasterly winds, the dispersion model results indicate that 9% of the time during the sugarcane fertilization season (in the modeled years 2001–2006) the meteorological conditions resulted in emissions from the coastal regions of north Queensland being transported out over the ocean around the Great Barrier Reef. The results suggest that there may be a greater efficiency for transport out over the reef during October than for November and December. For the 2 months that exhibited the greatest potential for transport of coastal pollution to the Great Barrier Reef, the modeled deposition of nitrogen oxides (NOX) into the Great Barrier Reef lagoon was less than 1% of the total emissions from the sugarcane plantations, but was not zero. Our model has a simple chemical scheme that does not cover the full chemistry of all reactive nitrogen compounds and so the results are only indicative of the potential levels of deposition. Nevertheless, our study shows that small amounts of NOX that originate from sugarcane fertilization may be transported and dry deposited into the Great Barrier Reef lagoon. Other pathways not included in the modeling scheme may provide a more efficient transport mechanism. Whilst modern practices for the application of fertilizer to sugarcane plantations have drastically reduced emissions, the potential efficiency of transport of pollutants via the atmosphere may be of concern for other more highly polluting agricultural industries.

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Transport of NO_X Emissions from Sugarcane Fertilisation into the Great Barrier Reef Lagoon

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Abstract.

The Great Barrier Reef World Heritage Area contains highly sensitive ecosystems that are threatened by the effects of anthropogenic activity including eutrophication. The nearby sugarcane plantations of tropical north Queensland are fertilised annually and there has been ongoing concern about the magnitude of the loss of applied nitrogen to the environment. Previous studies have considered the potential of rainwater run-off to deposit reactive nitrogen species into rivers and ultimately into the Great Barrier Reef Lagoon, but have neglected the possibility of transport via the atmosphere. This paper reports the results of a modelling study commissioned by the Australia's National Heritage Trust aimed at assessing whether or not

atmospheric deposition of reactive nitrogen from Queensland's sugarcane plantations posed a potential threat to the Great Barrier Reef Lagoon.

Atmospheric dispersion modelling was undertaken using TAPM (The Air Pollution Model), developed by Australia's Commonwealth Scientific and Industrial Research Organisation (CSIRO). Despite the predominance of onshore south easterly winds, the dispersion model results indicate that 9% of the time during the sugarcane fertilization season (in the modeled years 2001-2006) the meteorological conditions resulted in emissions from the coastal regions of north Queensland being transported out over the ocean around the Great Barrier Reef. The results suggest that there may be a greater efficiency for transport out over the reef during October than for November and December. For the two months that exhibited the greatest potential for transport of coastal pollution to the Great Barrier Reef, the modeled deposition of nitrogen oxides (NO_X) into the Great Barrier Reef lagoon was less than one percent of the total emissions from the sugarcane plantations, but was not zero. Our model has a simple chemical scheme that does not cover the full chemistry of all reactive nitrogen compounds and so the results are only indicative of the potential levels of deposition. Nevertheless, our study shows that small amounts of NO_X that originate from sugarcane fertilization may be transported and dry deposited into the Great Barrier Reef lagoon. Other pathways not included in the modeling scheme may provide a more efficient transport mechanism. Whilst modern practices for the application of fertilizer to sugarcane plantations have drastically reduced emissions, the potential efficiency of transport of pollutants via the atmosphere may be of concern for other more highly polluting agricultural industries.

Keywords: Great Barrier Reef, NO_X, Sugarcane, Ammonia, Atmospheric Transport, Deposition, Modelling, TAPM

1. Introduction

The Great Barrier Reef World Heritage Area contains highly sensitive ecosystems that are threatened by the effects of eutrophication. There have been a number of recent studies to determine the potential for rain-water run-off from the agricultural areas in Queensland to deposit reactive nitrogen into local waterways and to reach the vulnerable ecosystems of the Great Barrier Reef [*Brodie et al.*, 2004; *Cooper et al.*, 2007; *Haynes et al.*, 2007; *Luick et al.*, 2007; *Smith et al.*, 2008; *Wooldridge et al.*, 2006]. Evidence from these studies indicate that river-borne particulate material is typically trapped within 10km of the coast, whilst dissolved nutrients are dispersed much further, such that elevated nutrient concentrations are measurable at distances of hundreds of kilometres from river mouths (North and South) but due to the coastal currents the plumes are confined to a band up to 50km (East) of the coast [*Devlin et al.*, 2004]. As a result inner reef sites (close to the coast) are especially vulnerable to eutrophication whilst outer reef sites are protected [*Wooldridge et al.*, 2006]. Such increased dissolved nutrients have been cited as the cause of inhibited coral growth in areas near catchments with intensive agricultural activity [*Alongi et al.*, 2005].

None of these previous studies have assessed the potential for atmospheric transport of reactive nitrogen from the agricultural regions of Queensland to the Great Barrier Reef. One reason for this is that the measurement of atmospheric deposition of reactive nitrogen within the region is fraught with difficulties. This is because an island, reef or boat is required as a platform from which to make the measurements, but such a platform will attract birds with the result that the environmental measurements may be dominated by the effects of bird faeces rather than atmospheric transport of reactive nitrogen from regional sources. Australia's National Heritage Trust commissioned the modelling study reported in this paper to determine whether the

atmosphere might provide a significant transport route for reactive nitrogen from sugarcane plantations to the Great Barrier Reef. The reason that sugarcane is important in this region is that it is a major crop in tropical north Queensland, along the coastline closest to the Great Barrier Reef.

Nitrogen is applied annually as a fertiliser to most sugarcane plantations, most commonly in the form of urea. Some of the applied nitrogen is lost to the atmosphere in the form of gaseous nitrogen (N_2), ammonia (NH_3), nitric oxide (NO), nitrogen dioxide (NO_2) and nitrous oxide (N_2O). The purpose of the study described here is to model the atmospheric transport of the chemically reactive nitrogen compounds (NO, NO_2 and NH_3) to assess whether the release of these gases to the atmosphere from the fertilisation of sugarcane farming poses a significant risk to the waters within the Great Barrier Reef lagoon.

The Australian sugarcane industry is proactive in researching best practice. During the early 1990s several studies were undertaken to measure emissions of NH_3 from urea applied to sugarcane, which reported losses in the first 4-6 weeks after fertilization varying from 17% in very wet areas to as much as 39% of the applied nitrogen in drier zones [*Freney et al.*, 1992; *Prammanee et al.*, 1989; *Prasertsak et al.*, 2002]. These emissions from sugarcane occurred under a cultural system known as green cane harvesting in which harvesters separate the cane stalks from the trash (tops plus leaves) and return the trash to the soil surface [*Prasertsak et al.*, 2002]. The usual practice at that time was to apply fertiliser nitrogen as urea by broadcasting the fertiliser onto the trash surface. When the trash was wetted by dew, rain or condensation of evaporated soil water, some of the urea was dissolved and was rapidly hydrolysed by the urease enzyme present in the sugarcane residues. Because there are few sites for the absorption of ammonia in the trash, little of the ammonia was retained there and it was easily lost to the

atmosphere when the water evaporated [*Freney et al.*, 1992]. For a typical application of 160kg of nitrogen per hectare as urea, with 39% loss over the first six weeks [*Freney*, 1994; *Prasertsak et al.*, 2002] resulting emissions of NH_3 would be 1.5 kg-N $ha^{-1}d^{-1}$. In comparison, an emission rate equivalent to 10.6 kg-N $ha^{-1}d^{-1}$ of NH_3 has been reported from measurements spanning several weeks at a beef cattle feedlot in Queensland [*Denmead et al.*, 2008]. Whilst the emission rate from beef cattle feedlots is seven times larger than the emissions from sugarcane, the sugarcane plantations cover a much greater area of north Queensland than cattle feedlots and thus may still represent a major source of NH_3.

In the atmosphere, ammonia is a precursor to the formation of fine particulate matter, largely in the form of particulate ammonium (NH_4^+) in aerosols. Together, NH_3 and NH_4^+ are known as ammoniacal-nitrogen (NH_X). Airborne NH_X can be transported long distances, and is therefore a transboundary pollutant. *Asman and van Jaarsveld* [1992] indicated in a modeling approach that about half of the emitted ammonia is deposited as gaseous NH_3 while the remaining half is deposited by dry- or wet-deposition as NH_4^+ particles. Gaseous ammonia is deposited much closer to the source [*Dragosits et al.*, 2002; *Fowler et al.*, 1998; *Sutton et al.*, 1998]. Deposition studies around ammonia 'hot spots' using mass balance, ^{15}N labeling, and tracers as well as modeling have indicated that on land, the fraction recaptured by the surface within 2 km downwind from the source of NH_3 ranges from 2 to 60% [*Asman et al.*, 1998; *Loubet et al.*, 2006]. This localized deposition, which diminishes with increasing distance from the source, may affect plants growing nearby, result in excessive nitrogen accumulation in soils, and alter surface waters. It is known that when ammonium aerosols are washed out by precipitation, they can cause eutrophication of waterways on a regional scale adding unintended nitrogen to sensitive ecosystems, affecting biodiversity and other indicators of environmental

quality [*Asman et al.*, 1998; *Galperin et al.*, 1998; *Pearson et al.*, 1993]. Typical atmospheric concentrations of trace gases involved in NH_X chemistry in Queensland are not well documented in the scientific literature but are likely to be significantly lower than those experienced in the works cited here (that are predominantly from the relatively polluted European continent). Thus lack of knowledge of the atmospheric conditions is a major limitation to our ability to model the fate of ammonia emissions from sugarcane plantations in Queensland and any extrapolation of the conclusions from European studies should be considered indicative at best.

Green cane harvesting is currently the normal practice in most of the Queensland sugar belt, but now urea is usually applied in slits cut into the soil below the trash blanket so that the ammonia formed from urea hydrolysis is absorbed onto the exchange complex of the soil where it can be taken up by plant roots. This has proved to be highly effective in restricting ammonia emissions to the atmosphere. [*Prasertsak et al.*, 2002], for instance, found that drilling the urea into the soil to a depth of 5 to 10 cm reduced NH_3 emissions from around 37% of the nitrogen applied to close to 5%. More recent measurements from Mackay suggest that inserting the fertilizer at 10 – 15cm depth leads to further reduction in NH_3 emissions to approximately 0.3% over the entire growing season [*Wilson et al.*, 2008]. Such large reductions in nitrogen emissions are accompanied by substantial improvements in plant uptake, producing a significant financial benefit. Thus the practice of inserting the fertiliser to a depth of several centimetres has become more widespread amongst sugarcane farmers.

Historically, measurements of nitrogen losses to the atmosphere from sugarcane farming have focused on NH_3, but recently the first measurements of emissions that include nitric oxide (NO), nitrogen dioxide (NO_2) and nitrous oxide (N_2O) as well as ammonia (NH_3) have been reported [*Macdonald et al.*, 2009; *Wilson et al.*, 2008]. Measurements of emissions of these

nitrogen gases were made throughout both the 2006/2007 and the 2007/2008 growing seasons from a sugarcane crop in Mackay, north Queensland. Fertilisation followed the modern practice of inserting the fertiliser at a depth of approximately 10cm - 15cm. The net emissions of each gas were very similar in both years, with N_2O accounting for about 5 $kgNha^{-1}$ (3% of applied nitrogen), NO_X (NO and NO_2) accounting for about 1 $kgNha^{-1}$ (0.6% of applied nitrogen) and NH_3 for only about 0.5 $kgNha^{-1}$ (or 0.3% of applied nitrogen). This study by Macdonald *et al* [2009] indicates that N_2O and NO_X emissions are more likely to dominate the emissions of nitrogen from sugarcane plantations that use modern fertilisation practices. N_2O is an important greenhouse gas, but is not very reactive and therefore not of direct concern in terms of potential to cause eutrophication in the Great Barrier Reef lagoon. In contrast, atmospheric NO_X is chemically reactive, and is involved in both the production and consumption of atmospheric oxidants such as hydroxyl radicals and ozone. The main removal mechanisms for atmospheric NO_X are via the formation (and deposition of) nitric acid, and by direct deposition (both wet and dry). Since measurements of emissions from sugarcane plantations that utilise modern fertilisation methods suggest that NO_X is the dominant reactive nitrogen gas emitted [*Macdonald et al.*, 2009; *Wilson et al.*, 2008], our modelling study is focused on the atmospheric dispersion and deposition of NO_X. However, since previous measurements made after urea was applied to the top of the trash blanket showed much greater total emissions of reactive nitrogen species dominated by ammonia, care must be taken in extrapolating these recent results to the whole north Queensland sugarcane belt.

2. Description of the Atmospheric Dispersion Model

The model used in this study was the atmospheric dispersion model known as TAPM V3 (The Air Pollution Model - Version 3), developed by Australia's Commonwealth Scientific and Industrial Research Organisation (CSIRO) to run on a normal personal computer [*Hurley et al.*, 2005]. TAPM was designed to allow companies to meet their obligations to Environmental Protection Agencies by enabling them to predict the concentrations of pollutants emitted by their industries in the local environment. It has performed well in a number of verification studies [*Edwards et al.*, 2004; *Hurley*, 2000; *Hurley et al.*, 2003; *Hurley et al.*, 2001; *Luhar et al.*, 2003; 2004]. Brief technical details of the model are given here - for greater detail see [*Hurley et al.*, 2005].

TAPM uses synoptic analyses to set-up large-scale meteorological fields and then predicts the airflows important to the smaller scale, (such as sea breezes or terrain induced flows), by solving approximations to the fundamental fluid dynamics and scalar transport equations. The model solutions for winds, specific humidity and potential virtual temperature are periodically adjusted towards the synoptic analyses values.

TAPM includes databases of synoptic analyses of meteorological data, terrain, vegetation and soil type and sea-surface temperature. The databases used in the configuration of TAPM described in this study are:

1. six-hourly synoptic scale analyses from the Australian Bureau of Meteorology on a longitude/latitude grid at 0.75- or 1.0-degree grid spacing (approximately 75 km or 100 km);
2. Australian terrain height data from Geoscience Australia on a longitude/latitude grid at 9-second grid spacing (approximately 0.3 km);

3. Australian vegetation and soil type data from CSIRO Wildlife and Ecology on a longitude/latitude grid at 3-minute grid spacing (approximately 5 km) and
4. global long-term monthly mean sea surface temperatures from the US National Center for Atmospheric Research on a longitude/latitude grid at 1-degree grid spacing (approximately 100 km).

The air pollution component in TAPM has both a Lagrangian particle module and a Eulerian grid module. It is this latter module that is of interest for the regional scale modeling described in this study. It calculates concentration fields for the chosen grid area given the relevant emissions and background concentrations of key chemical species. The model includes representations of advection, diffusion, chemical reactions and wet and dry deposition processes.

TAPM can be run in tracer mode or in chemistry mode. In the tracer mode the model uses emission rates of the given tracer(s) and calculates the dispersion that results from advection and diffusion but there is no representation of chemical processes except that an atmospheric lifetime can be set for the tracer. The tracer mode is computationally faster than the chemistry mode and is useful for determining approximate dispersion patterns of emitted gases that are not very chemically reactive. In chemistry mode, nitric oxide (NO), nitrogen dioxide (NO_2), ozone (O_3), sulphur dioxide (SO_2) and hydrogen peroxide (H_2O_2) are represented along with eight composite species; the radical pool (RP), smog reactivity (Rsmog), stable non-gaseous organic carbon (SNGOC), stable gaseous nitrogen products (SGN), stable non-gaseous nitrogen products (SNGN), stable non-gaseous sulphur products (SNGS), plus Airborne Particulate Matter (APM) and Fine Particulate Matter (FPM). Ten chemical reactions are included that link the 13 species and these are listed in Table 1. Dry deposition calculations are based upon *Wesely* [1989] with

deposition velocities for the different gases from *Wesely* [1989] and *Harley et al* [1993]. The model represents the major chemical processes for atmospheric nitrogen oxide (NO) and nitrogen dioxide (NO_2) but has no representation of ammonia (NH_3).

TAPM has some significant limitations for this modelling study including the lack of NH_3 chemistry and the use of composite species typically in the chemistry mode. There are global chemical transport models available that have a much more complex representation of reactive nitrogen chemistry but these have very low spatial resolution and therefore cannot capture the detailed regional transport required for the study. Ideally detailed inventories of the sources and sinks of all relevant trace gases for regional Queensland would be included in the full chemistry model of reactive nitrogen in the local atmosphere. However such information is not readily available for rural Australia. TAPM provides the spatial resolution to model the dispersion of nitrogen species from the sugarcane plantations and assess the likelihood of transportation to the Great Barrier Reef lagoon. However, since TAPM has a simplified chemical reaction scheme with the chemical state of the atmosphere controlled by maintaining the background levels of the species represented, the deposition results are only indicative of the potential levels reaching the reef.

3. Modelling the Dispersion of a Tracer from Sugarcane Plantations near the Queensland Coast

3.1 Model Set-up

The prevailing winds in the sugarcane growing region of Queensland on Australia's northeast coast are south easterlies and so the expectation is that most of the emissions will be blown inland. The initial modeling exercise was aimed at understanding how often and to what extent

the local meteorological conditions result in emissions from the sugarcane plantations being transported out over the Great Barrier Reef Lagoon.

The location of sugarcane fields was obtained from a land use dataset for Queensland supplied by the Queensland Government's Department of Natural Resources and Water. The data set was supplied in the geocentric datum of Australia (GDA_94) geographical co-ordinate system as a series of polygons defining land use. The centre points and area of all polygons representing either irrigated or non-irrigated sugarcane fields were calculated using the Universal Transverse Mercator projection. The projection of the curved surface of the Earth onto a flat reference grid necessarily results in some distortion to the location and area of the sugarcane fields, with the distortion increasing with distance from the central line of the longitudinal zone. In this case the resulting distortion to the true area has been calculated to be less than 0.5%. Each polygon was included in the model as a point source at its centre point and an emission rate calculated by multiplying the area of the polygon in hectares with the appropriate emission rate per hectare of the gas being modelled.

TAPM allows up to 5 different grids resolutions, with the finer grids nested in the larger grids. A separate grid can be used to examine the pollution levels predicted by the model. This allows the large-scale meteorological input to be used as well as very fine detail around the source of emissions and around the area in which the pollution levels are of interest. In our model study we have a very large area of sources (spanning the main sugarcane growing areas in Queensland), and we are interested in the resulting pollution levels over large areas of the Great Barrier Reef lagoon. For this reason we used a single 10km by 10km grid spacing centred on Mackay (latitude = 21º08' South, longitude = 149º11' East) and extending to a total area of 1000km by 1000km.

The same grid was used to analyse the resulting pollution levels. The TAPM model grid is shown in Figure 1, the locations of the sugarcane plantations marked in white.

Fertilisation of sugarcane in Queensland usually occurs sometime in the last 3 months of the calendar year with most of the nitrogen losses to the atmosphere occurring in the few weeks following fertilisation [*Freney et al.*, 1992; *Prammanee et al.*, 1989; *Prasertsak et al.*, 2002]. This model study was composed of eighteen separate model runs, each of one month duration for every October, November and December in each of six years (2001 – 2006) of the study. Each model run simulated the scenario that all of the sugarcane fields in Queensland were fertilized together at the start of the month and emitted a tracer at a constant emission rate. The model runs last for one month each and produce hourly calculated tracer concentration fields.

3.2 Results of Tracer Model Runs

Despite prevailing easterly winds, the model output predicted frequent incursions of tracer plumes over the ocean in the vicinity of the Great Barrier Reef. Tracer plumes that extended out over the ocean beyond 50km from the coastline were counted as significant incursions because atmospheric deposition near the coast is likely to be insignificant in comparison to runoff of sediments and nutrients from rivers [*Devlin et al.*, 2005a].

A small number of individual sites of interest within the reef were chosen to represent typical outer reef sites, (Flora Reef, Abington Reef and Swain Reefs) or typical inner reef sites (Slashers Reef, Hook Reef, Sandpiper Reef and Heron Island), and the concentrations of tracer reaching those particular sites were examined in more detail (see Figure 1).

Table 2 summarises the results of individual tracer model runs, showing:

1. the total number of hours in each month that have significant incursions (when tracer plumes are transported out over the ocean with a maximum extent of approximately 50km or more from the coastline)
2. the percentage of time that tracer plumes incursions occur
3. the mean monthly tracer concentration for the inner reef (averaged from the four inner reef sites) and
4. the mean monthly tracer concentration for the outer reef (averaged from the three outer reef sites).

Despite the predominance of south easterly winds the dispersion model results indicate that on average 9% of the time during the sugarcane fertilization season (October through to December) the meteorological conditions are such that emissions from the coastal regions of Northern Queensland are transported to the Great Barrier Reef lagoon. On average the efficiency of tracer transport to the outer reef is 13% of the efficiency of transport to the inner reef.

One potentially interesting question is whether the transport efficiency is different for different months of the year. In Table 3 the monthly mean results from October each year have been averaged together, and compared to the monthly means for November and December from 2001 to 2006 inclusive. The data are taken from model runs encompassing only six years, however the results suggest that there may be a greater efficiency for transport out over the reef during October than for November and December. If this is the case then delayed fertilization should be encouraged in the sugarcane industry and other agricultural industries in Northern Queensland in order to minimize the impact on the Great Barrier Reef.

4. Modelling the Deposition of NO and NO_2 Emissions from Sugarcane Plantations into the Great Barrier Reef Lagoon

4.1 Model Description

A second study focused on the two months from the tracer model runs which showed the most significant transport of pollution from the sugarcane plantations to the Great Barrier Reef lagoon. These months were October 2001 and November 2003. TAPM was configured as before with a 10km by 10km grid spacing centred on Mackay and extending to a total area of 1000km by 1000km with the locations of all the sugarcane plantations included. Again each model run simulated the scenario that all of the sugarcane fields in Queensland were fertilized together but this time TAPM was run in chemistry mode to model the fate of emitted NO_X and the subsequent deposition into the Great Barrier Reef lagoon.

The only measurements of NO_X emissions from sugarcane of which we are aware are reported in *Denmead et al* [2005] (from two separate sites) and *Wilson et al* [2008] (from one site). The first set of measurements was taken over 13 days from an area where soybeans had been harvested just prior to the sugarcane being planted (but with no additional fertilization) and yielded a relatively high average emission rate of NO_X of 0.24 kg-N $ha^{-1}d^{-1}$ [*Denmead et al.*, 2005]. The second set of measurements was from a nearby site that was fertilized with 50kg urea per hectare midway through the 13 days of measurements and the average emission rate of NO_X was an order of magnitude lower at 0.025 kg-N $ha^{-1}d^{-1}$, although in the 3 days following fertilization the measured emission rate of NO_X was approximately 0.10 kg-N $ha^{-1}d^{-1}$[*Denmead et al.*, 2005]. The third set of measurements was from a sugarcane plantation in Mackay during the first six weeks following fertilization with urea inserted into slots at a depth of 10 – 15 cm depth and produced a similar figure of 0.018 kg-N $ha^{-1}d^{-1}$ [*Wilson et al.*, 2008].

The very large variation in the measured emission rates and the short time span of the first two sets of measurements (only 13 days) make it hard to interpret how representative these measurements might be. Another comparison can be made with published values for emissions of NO from a variety of non-legume crops of 0.5% of applied nitrogen lost as NO over the complete growing season [*Veldkamp et al.*, 1997]. If we assume that 160kg of nitrogen per hectare is applied and that the 0.5% is emitted in the first month after fertilization we get an equivalent emission rate of 0.027 kg-N $ha^{-1}d^{-1}$. Thus it seems that the emissions from soils previously used to grow legumes are an order of magnitude higher than sites fertilsed with urea. However we wish to determine an upper limit for the atmospheric transportation of reactive nitrogen to the Great Barrier Reef so the highest reported emission rate for NO_X of 0.24 kg-N $ha^{-1}d^{-1}$ is used [*Denmead et al.*, 2005]. Each sugarcane plantation was included in the model as a point source emitting NO_X at a constant rate. The model assumed a partitioning of 75% NO and 25% NO_2 for emitted NO_X as measured in Mackay [*Wilson et al.*, 2008].

No other emissions are included in the model. Instead the composition of the atmosphere is maintained by specifying background mixing ratios of the relevant species included in the chemical scheme. The following background mixing ratios of were chosen after a private communication from *Martin Cope, CSIRO* and with reference to *Warneck* [2000]: Rsmog = 0.2 nmol mol^{-1} , NO_X = 0.2 nmol mol^{-1} , SO_2 = 0.0 nmol mol^{-1} , O_3 = 16 nmol mol^{-1} , APM = 10 μg m^{-3} and FPM = 5 μg m^{-3}.

4.2. Results from Modelling the Deposition of NO and NO_2 Emissions into the Great Barrier Reef Lagoon

The model output is summarised graphically for October 2001 in Figure 2 and for November 2003 in Figure 3. For illustrative purposes a threshold value is set for each output parameter at 1% of the maximum value obtained for any grid space throughout each model run.

Two plots are shown in Figure 2 and Figure 3 indicating grid spaces where (a) the mean monthly concentration and (b) the total monthly dry deposition of NO_X exceed 1% of their maximum values for the month-long model run. During October 2001 the area with monthly average atmospheric NO_X concentrations greater than 1% of maximum encompasses Hook Reef and extends almost to Sandpiper Reef as can be seen in Figure 2Figure 2a. The area with values for the total monthly dry deposition of NO_X greater than 1% of the maximum value within the modeled region, extends less far over the ocean as illustrated by Figure 2b. In contrast the area with monthly average NO_X concentrations greater than 1% of maximum during November 2003 does not extend as far to the east around the Mackay area as it did in October 2001 (see Figure 3a). Similarly the area with monthly average NO_X dry deposition values greater than 1% of the maximum in the modeled region in November 2003, is confined to regions close to the coast or to the west of the sugarcane growing regions (see Figure 3b).

Table 5 and Table 6 show the modelled average mixing ratio of NO_X in $nmol.mol^{-1}$during October 2001 and November 2003 respectively alongside the dry deposition of NO_X in kg-N $ha^{-1}d^{-1}$ at the chosen sites of interest. Also given is the dry deposition in the 10km by 10km grid box containing the site of interest expressed as a percentage of the total amount of nitrogen emitted as NO_X. In addition to the four inner reef sites (Hook Reef, Heron Island, Sandpiper Reef and Slashers Reef) and three outer reef sites (Flora Reef, Swain Reef and Abington Reef) used for the tracer study, we looked at dry deposition in the model grid squares that contained two sites just off the coast in the central section of the Great Barrier Reef lagoon (Rockingham Bay and

Missionary Bay). These sites were included because deposition rates of nitrogen into coastal sediments and fluxes from sediments back into the coastal waters have been reported at these places [*Alongi and McKinnon*, 2005], allowing a comparison to be made with the modeled atmospheric fluxes. The locations of Rockingham Bay and Missionary Bay are shown in figure 4. The towns of Cairns, Townsville, Mackay, Gladstone and Bundaberg are also included so that a contrast can be made between coastal sites near major sugarcane regions (Mackay, Bundaberg and Cairns) and sites further away (Townsville and Gladstone).

A deposition of particulate nitrogen into the top 20cm of the coastal sediment equivalent to 0.46 kg-N $ha^{-1}d^{-1}$ has been reported for Rockingham Bay along with flux rates from the sediment into the ocean of 0.029 kg-N $ha^{-1}d^{-1}$ of NH_4^+ and 0.0049 kg-N $ha^{-1}d^{-1}$ of NO_2^- and NO_3^- [*Alongi and McKinnon*, 2005]. At Missionary Bay a deposition of particulate nitrogen equivalent to 0.69 kg-N $ha^{-1}d^{-1}$ has been reported in the same study along with a flux rate from the sediment into the ocean of 0.13 kg-N $ha^{-1}d^{-1}$ of NH_4^+ and a deposition rate into the sediment of 0.018 kg-N $ha^{-1}d^{-1}$ of NO_2^- and NO_3^-.

In comparison, the modeled deposition rates of NO_X from the atmosphere into the ocean are:

- approximately 0.0043 kg-N $ha^{-1}d^{-1}$ and 0.0018 kg-N $ha^{-1}d^{-1}$ at Rockingham Bay in October 2001 and November 2003 respectively, and
- approximately 0.0025 kg-N $ha^{-1}d^{-1}$ and 0.0010 kg-N $ha^{-1}d^{-1}$ at Missionary Bay in October 2001 and November 2003 respectively.

Thus the modeled deposition rates of NO_X from the atmosphere into the ocean are approximately two orders of magnitude smaller than the total particulate nitrogen deposition into coastal sediments and in most cases significantly smaller than the exchange rates between ocean and

sediment. Only at Rockingham Bay in October 2001 (of 0.0043 kg-Nha^{-1}d^{-1}) is the modeled atmospheric NO_X deposition comparable to the measured flux rate of NO_2^- and NO_3^- (of 0.0049 kg-Nha^{-1}d^{-1}) from the sediment into the ocean. Thus we can conclude that for these sites close to the coast and river mouth, the deposition of NO_X from emissions from sugarcane fertilization are typically less significant than deposition from river borne N particulates. Compared to these coastal sites, deposition rates are more than an order of magnitude smaller at the inner reef sites (2.3 x 10^{-4} kg-Nha^{-1}d^{-1} in October 2001 and 1.1 x 10^{-4} kg-N ha^{-1}d^{-1} in November 2003) and two orders of magnitude or more smaller at the outer reef sites (2.1 x 10^{-5} kg-N ha^{-1}d^{-1} in October 2001 and 4.3 x 10^{-6} kg-Nha^{-1}d^{-1} in November 2003). In contrast, the towns near major sugarcane growing areas, Mackay and Bundaberg have deposition rates an order of magnitude higher than the coastal sites, showing a tendency for emitted NO_X to deposit close to the source.

Table 5 and Table 6 also show the dry deposition of NO_X (in kg-N d^{-1} and expressed as a percentage of the total amount of nitrogen emitted as NO_X) for the whole model area, the area covered by sea and the area of sea greater than 50km east of the coast. In both months approximately 15% of the emitted NO_X was dry deposited somewhere in the modeled region within the month of the model run, with the remainder being either transported out of the region, or retained in the atmosphere. The mean fraction of the total emitted nitrogen that is deposited in the grid spaces containing the four inner reef sites during October 2001 is 5.4x10^{-4}% and during November 2003 is 2.6 x10^{-4}%. It should be noted that this is the percentage of the total emitted nitrogen that is deposited into a single 10 km by 10 km grid square. In comparison the total deposition into the sea within the model was 1.6% and 1.0% of the total emitted nitrogen for October 2001 and November 2003 respectively. We also considered the deposition into an area of sea defined by being at least 50km east of the coast. This is of potential interest since river

borne sediment deposition has been shown to be contained within an area approximately 50km from the shore [*Devlin et al.*, 2005b], so deposition from the atmosphere is likely to be more significant in the total budget in regions further from the coastline. The total deposition into the model area of sea that was greater than 50km east of the coast was 0.5% and 0.7% of the total emitted nitrogen for October 2001 and November 2003 respectively. Also worthy of note is that despite a lower total deposition into sea in November 2003 than in October 2001, the deposition into the region beyond 50km was greater both as an absolute and as a percentage of the total emissions.

7. Discussion

The two model runs for NO_X transport predicted that less than 1% of the NO_X emitted from the sugarcane plantations will be deposited into the Great Barrier Reef lagoon (or the area of model covered by sea further than 50km east of coastline). The <1% deposition occurs over a very large area (453,000 km) and the two months of the model runs were chosen specifically for their meteorological conditions that favoured transport to the reef. Thus by assuming the low emission rates of total reactive nitrogen from sugarcane plantations that have adopted modern fertiliser practices and the dominance of NO_X in these emissions [*Macdonald et al.*, 2009; *Wilson et al.*, 2008], we infer a level of reactive nitrogen deposition that is unlikely to constitute a serious threat to the reef. However the modelled scenario neglects the potential deposition of other reactive nitrogen species such as ammonia and ammonium (NH_X) to the reef. Since ammonia emissions can be substantial if the fertiliser is not buried below the surface then this omission could substantial alter the conclusions of the study. Furthermore NH_X may be more

easily transported than NO_X and has higher deposition velocities [*Poor et al.*, 2001] and so efficiency of transport to the Great Barrier Reef lagoon is likely to be higher.

The results of the tracer model runs showed that although the dominant wind direction was onshore the conditions required to transport pollution from the agricultural regions to the Great Barrier Reef were not unusual and occurred approximately 9% of the time. These tracer runs can also give us a qualitative indication of ammonia transportation from the sugarcane plantations to the reef. The tracer emission rate is equivalent to that typical for ammonia for the old practice of applying the fertiliser by broadcasting onto the trash surface, (40% of applied nitrogen lost as ammonia in the first 6 weeks at 160kg of nitrogen per hectare as urea, equates to 1.5 kg-N $ha^{-1}d^{-1}$). The concentrations given in Table 2 for the mean tracer concentration at the inner and outer reef sites may be converted to $nmol.mol^{-1}$ producing mixing ratios for NH_X that are approximately twice those reported for NO_X. Thus the NH_X branch may provide greater potential for transport of emitted reactive nitrogen from sugarcane to the Great Barrier Reef Lagoon.

8. Summary and Conclusions

Two modelling studies were undertaken to assess the potential transport of volatilised nitrogen emissions from north Queensland sugarcane plantations to the Great Barrier Reef lagoon. The first modeling study used an atmospheric dispersion model to estimate how often and to what extent the local meteorological conditions result in emissions from the sugarcane growing areas being transported over the ocean. A second modeling study examined the transport of NO_X emitted from the sugarcane fields and the resulting dry deposition of NO_X at individual sites within the Great Barrier Reef.

The main conclusions of these modelling studies are:

1. Despite the predominance of south easterly winds the dispersion model results indicated that 9% of the time during the sugarcane fertilization season (October through to December) the meteorological conditions are such that emissions from the coastal regions of Northern Queensland are transported out over the ocean.

2. On average the efficiency of tracer transport to the outer reef is 13% of the efficiency of transport to the inner reef.

3. The results of the tracer dispersion modeling suggest that there may be a greater efficiency for transport out over the reef during October than for November and December. If this is the case in general then delayed fertilization should be encouraged in the sugarcane industry and other agricultural industries in Northern Queensland in order to minimize the impact of atmospheric transport of nitrogen emissions to the Great Barrier Reef.

4. The modeled deposition rates of NO_X from the atmosphere into the ocean are small and for two sites close to the coast (Missionary Bay and Rockingham Bay) the deposition of NO_X originating from sugarcane fertilization were significantly lower than the deposition from river borne particulates reported in the literature.

5. Deposition rates are more than an order of magnitude smaller at the inner reef sites than at the coastal sites (of Missionary Bay and Rockingham Bay) and two orders of magnitude smaller at the outer reef sites.

6. The total modeled deposition into the sea as NO_X within the model was 1.6% and 1.0% of the total emitted nitrogen for October 2001 and November 2003 respectively, the two

months with the greatest efficiency for transporting emissions from the sugarcane areas to the Great Barrier Reef.

7. The total deposition into the model area of sea that was greater than 50km east of the coast was 0.5% and 0.7% of the total emitted nitrogen for October 2001 and November 2003 respectively.

The modelling studies showed that transport of emitted NO_X from the Queensland coast into the Great Barrier Reef lagoon was limited to less than one percent of total emissions, but was not zero. TAPM cannot precisely reproduce all the relevant chemical and physical processes that occur in the atmosphere, and the simplifications inherent in the model may introduce some significant biases in the results for efficiency of transport of NO_X. These uncertainties in the model are not readily quantifiable, but the uncertainty in total deposition rates of NO_X are probably dominated by the uncertainty in the magnitude of emissions as evidenced by the large spread of emission rates reported in the literature.

Our overall conclusion is that atmospheric transport of pollution from the agricultural regions on the Queensland coast is small but not negligible. Recent measurements suggest that modern practices for the application of fertilizer to sugarcane plantations are such that volatized nitrogen emissions from this source have been dramatically reduced. Nevertheless the NHX branch missing in our model may provide a more efficient transport route from the Queensland coast to the Great Barrier Reef Lagoon. Emission rates reported in the literature suggest that ammonia from cattle farming and other agriculture in tropical north Queensland could be more significant than emissions from sugarcane plantations. Further measurements of emissions from other types of agriculture in the region are therefore recommended along with better characterisation of

regional sources and sinks of atmospheric gases that may allow a more thorough modelling study to be conducted.

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Figures

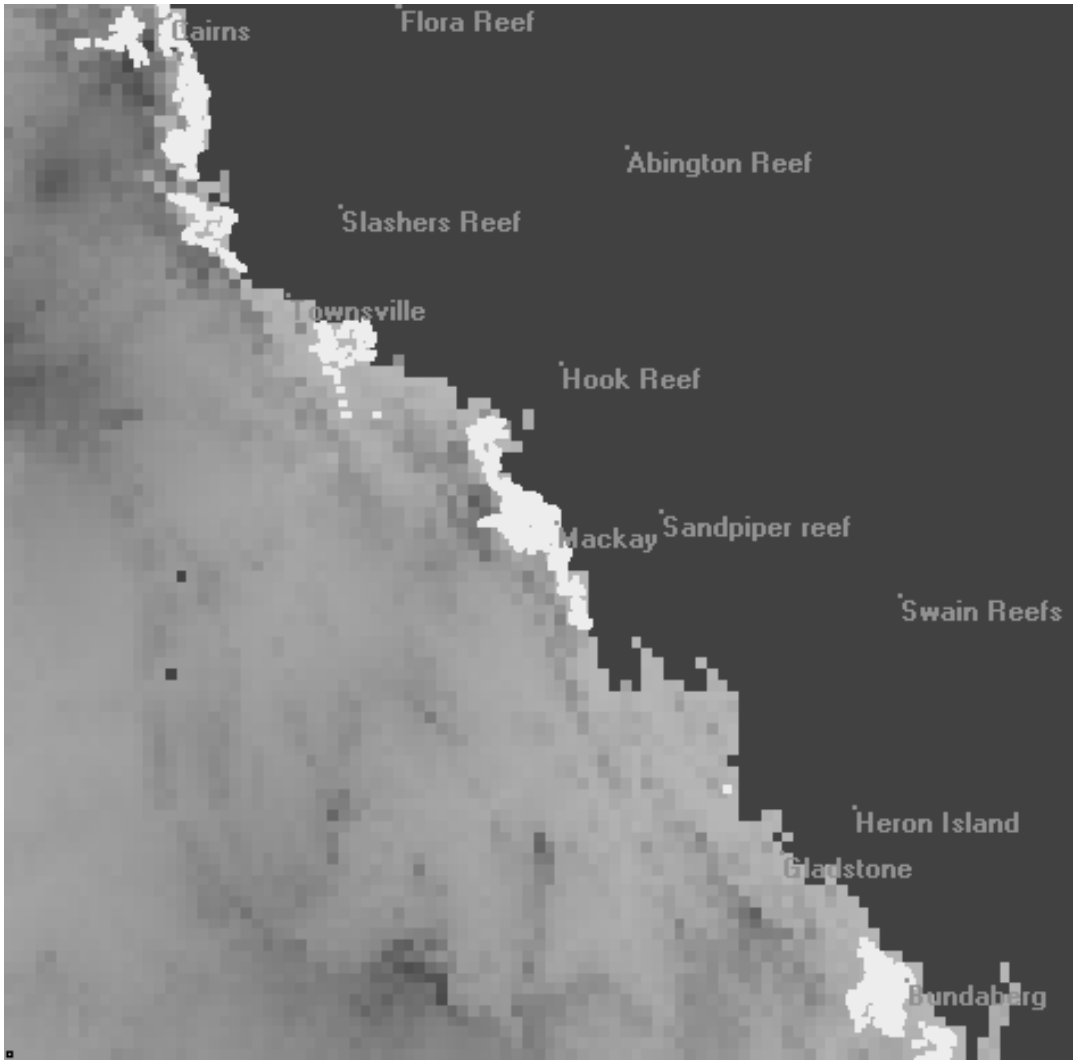

Figure 1 The TAPM modelled area, 1000km by 1000km centred on Mackay. Each pixel represents a 10km by 10km grid box. The locations of sugarcane plantations are shown in white.

(a) Oct 2001: - Monthly average NO_X > 0.48nmol .mol^{-1}

(b) NO_X Dry deposition > 59 µmol m^{-2} d^{-1}

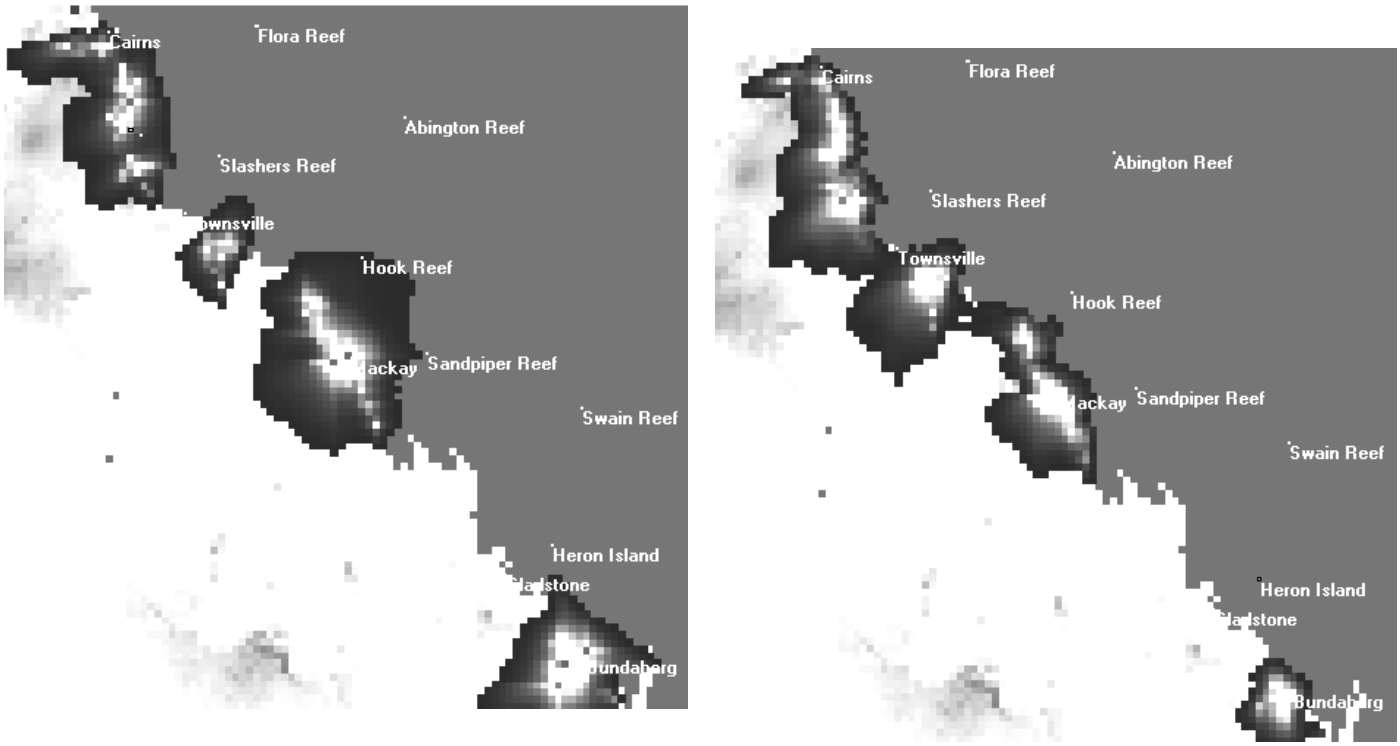

Figure 2 (a) A plot to show grid spaces where the mean monthly mixing ratio is greater than 0.48 nmol mol^{-1} (48 nmol mol^{-1} was the highest mean monthly NO_X concentration of any grid space during October 2001). (b) A plot to show grid spaces where the total monthly dry deposition of NO_X exceeds 59 µmol m^{-2} d^{-1}. The dark grey regions around the sugarcane growing areas on the coast represent 1% of maximum (0.48 nmol mol^{-1}) in (a) and 59 µmol m^{-2} d^{-1} in (b) with the white and mid-grey encompassed in these regions representing increasing values. The mid-grey to the left and the white to the right are areas of the sea and land respectively where the mixing ratio and deposition are less than 1% of the maximum values.

(a) Nov 2003: - Monthly average NO_X > 0.38nmol mol^{-1}

(b) NO_X Dry deposition > 52 µmol m^{-2} per d^{-1}

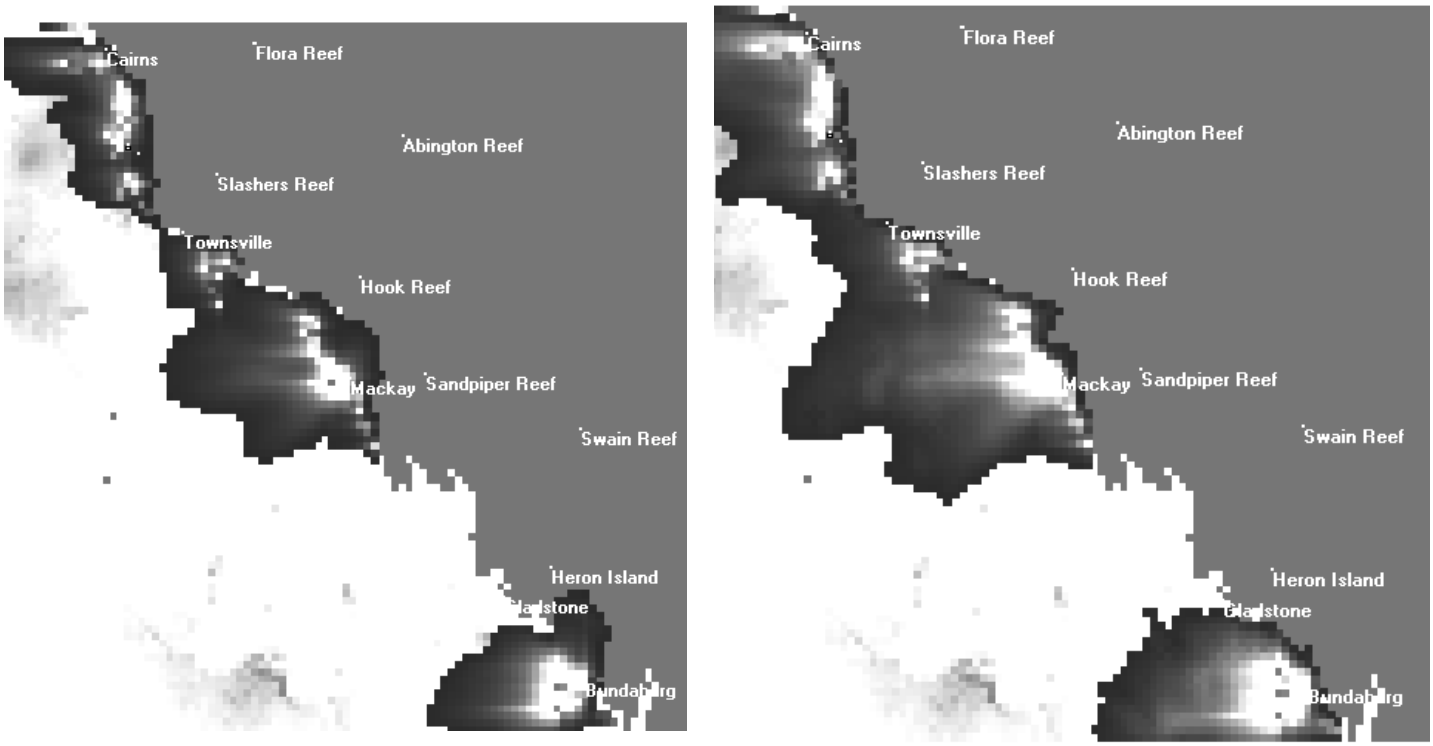

Figure 3 (a) A plot to show grid spaces where the mean monthly mixing ratio is greater than 0.38 nmol mol^{-1} (38 nmol mol^{-1} was the highest mean monthly NO_X concentration of any grid space during November 2003). (b) A plot to show grid spaces where the total monthly dry deposition of NO_X exceeds 52 µmol m^{-2} d^{-1}. The dark grey regions around the sugarcane growing areas on the coast represent 1% of maximum (0.38 nmol mol^{-1}) in (a) and 52 µmol m^{-2} d^{-1} in (b) with the white and mid-grey encompassed in these regions representing increasing values. The mid-grey to the left and the white to the right are areas of the sea and land respectively where the mixing ratio and deposition are less than 1% of the maximum values.

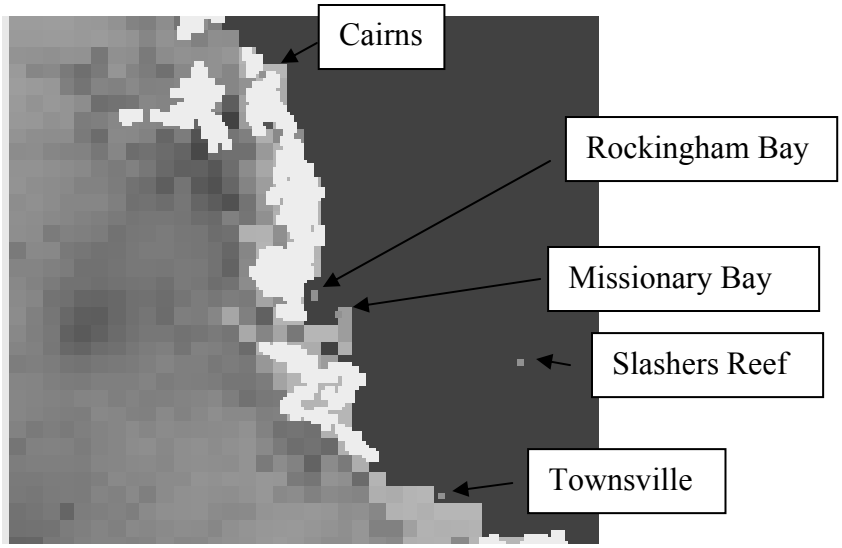

Figure 4 Shows the location of Missionary Bay and Rockingham Bay

Tables

Table 1 Chemical reactions used in TAPM for gases and composite species, where ή and α are yield coefficients.

$R_{smog} + hv \Rightarrow RP + R_{smog} + ήSNGOC$
$RP + NO \Rightarrow NO_2$
$NO_2 + hv \Rightarrow NO + O_3$
$NO + O_3 \Rightarrow NO_2$
$RP + RP \Rightarrow RP + \alpha H_2O_2$
$RP + NO_2 \Rightarrow SNG$
$RP + NO_2 \Rightarrow SNGN$
$RP + SO_2 \Rightarrow SNGS$
$H_2O_2 + SO_2 \Rightarrow SNGS$
$O_3 + SO_2 \Rightarrow SNGS$

Table 2. Column 1 shows the total number of hours in each month that TAPM predicts that tracer plumes are transported out over the ocean with a maximum extent of approximately 50km or more from the coastline. The number of hours is also given as a percentage of the total number of hours in the month in column 2. The mean monthly concentrations from the four inner reef sites are averaged to give a mean concentration in μgm^{-3} for the inner reef (column 3) and the mean monthly concentration from the three outer reef sites is averaged to give a mean concentration in μgm^{-3} for the outer reef (column 4).

	Incursions (hours per month)	Incursions % of time	Mean concentration inner reef (μgm^{-3})	Mean concentration outer reef (μgm^{-3})
Oct-01	232	31.2	0.795	0.070
Nov-01	132	18.3	0.177	0.020
Dec-01	103	13.8	0.091	0.051
Oct-02	57	7.7	0.082	0.017
Nov-02	0	0.0	0.000	0.000
Dec-02	61	8.2	0.067	0.008
Oct-03	126	16.9	0.205	0.037
Nov-03	110	15.3	0.344	0.041
Dec-03	48	6.5	0.081	0.001
Oct-04	60	8.1	0.124	0.001
Nov-04	17	2.4	0.002	0.000
Dec-04	36	4.8	0.058	0.002
Oct-05	77	10.3	0.116	0.003
Nov-05	23	3.2	0.005	0.003
Dec-05	67	9.0	0.142	0.022
Oct-06	20	2.7	0.000	0.000
Nov-06	47	6.5	0.046	0.022
Dec-06	0	0.0	0.000	0.000
All times	1216	9.2	0.130	0.017

Table 3 shows the percentage of the time that meteorological conditions result in significant incursions; the mean concentration in nmol mol^{-1} from the four inner reef sites and the mean concentration in nmol mol^{-1} from the three outer reef sites

	Incursions % time	Mean concentration inner reef (nmol mol^{-1})	Mean concentration outer reef (nmol mol^{-1})
All Octobers (2001 – 2006)	12.8	0.29	0.03
All Novembers (2001 – 2006)	7.6	0.14	0.02
All Decembers (2001 – 2006)	7.1	0.11	0.02

Table 4: modelled NO_X mixing ratios and dry deposition rates at several sites of interest in the Great Barrier Reef Lagoon and along the Queensland Coast during October 2001.

Location	Mean mixing ratio NOx (nmol mol^{-1})	Dry Deposition NOx (kg-N $ha^{-1}d^{-1}$)	% of total emitted N deposited in grid box
Hook Reef	0.51	0.00035	0.00081
Heron Island	0.29	0.00022	0.00052
Sandpiper Reef	0.44	0.00029	0.00068
Slashers Reef	0.10	0.00006	0.00015
Flora Reef	0.07	0.00004	0.00009
Swain Reef	0.04	0.00001	0.00003
Abington Reef	0.02	0.00001	0.00003
Cairns	0.74	0.00205	0.0048
Townsville	0.15	0.00025	0.0006
Mackay	15.86	0.02667	0.0624
Gladstone	0.16	0.00037	0.0009
Bundaberg	17.81	0.03097	0.0725
Missionary Bay	1.01	0.00245	0.0057
Rockingham Bay	3.67	0.00430	0.0101
		Dry Deposition NOx kg-N d^{-1}	**% of total emitted N deposited in grid box**
Whole Model Area		66418	15.5
All Sea		6816	1.6
Sea >50km East of Coast		2264	0.5

Table 5 modelled NO_X mixing ratios and dry deposition rates at several sites of interest in the Great Barrier Reef Lagoon and along the Queensland Coast during November 2003.

Location	Mean mixing ratio NOx (nmol mol^{-1})	Dry Deposition NOx (kg-N $ha^{-1}d^{-1}$)	% of total emitted N deposited in grid box
Hook Reef	0.16	0.000089	0.00021
Heron Island	0.28	0.000183	0.00043
Sandpiper Reef	0.17	0.000093	0.00022
Slashers Reef	0.10	0.000074	0.00017
Flora Reef	0.02	0.000006	0.00001
Swain Reef	0.05	0.000004	0.00001
Abington Reef	0.02	0.000002	0.00001
Cairns	0.53	0.00112	0.0026
Townsville	0.35	0.00056	0.0013
Mackay	5.13	0.00928	0.0217
Gladstone	0.08	0.00017	0.0004
Bundaberg	8.00	0.01761	0.0412
Missionary Bay	0.49	0.00101	0.0024
Rockingham Bay	1.49	0.00180	0.0042
		Dry Deposition NOx kg per day	**% of total emitted N deposited in grid box**
Whole Model Area		59420	13.9
All Sea		4365	1.0
Sea >50km East of Coast		2866	0.7