## CHAPTER 23

# THE PHYSICAL OCEANOGRAPHY OF SINGAPORE COASTAL WATERS AND ITS IMPLICATIONS FOR OIL SPILLS

## ENG SOON CHAN, PAVEL TKALICH, KARINA YEW-HOONG GIN, AND JEFFREY P. OBBARD

## 1. INTRODUCTION

The island of Singapore (Figure 1) is strategically located at the crossroads of major shipping routes which link the Indian Ocean to the South China Sea. In 2004, the TEUs Port of Singapore handled 20.6 million in Singapore (www.internationalpsa.com) and approximately 140,000 vessels call at the port annually (www.mpa.gov.sg). At any one time, it is estimated that some 800 ships are distributed in Singapore port waters. From an environmental perspective, one of the challenges which port managers face is the increased risk of accidents due to the heavy shipping traffic coupled with a busy port.

In past decades, accidents have occurred occasionally, including the collision between the *Evoikos* and *Orapin Global* in 1997 which spilled 28,500 tonnes of marine fuel oil into the Singapore Strait. Singapore is also one of the largest oil refining centres of the world, with a capacity to process more than one million barrels, or approximately 137,000 tonnes of crude oil daily. The associated chemical and petrochemical industries are crucial sectors of the Singapore economy. Along with the rapid growth of the Asian economy, hence contributing to the increased shipping and port activities, the ability to minimize the risk of accidents and to track and protect the marine environment are just as critical. This would require both the development and implementation of technologies and the enhanced understanding of the physical, chemical and biological processes of the waters around Singapore.

In this chapter, an overview of the physical oceanography of Singapore coastal waters is described. Implications on transport processes with focus on the impacts of oil spills and baseline persistent organic pollutants are discussed.

*E. Wolanski (ed.), The Environment in Asia Pacific Harbours*, 393–412 © 2006 Springer. Printed in the Netherlands.



Figure 1. Bathymetry (depth in m) of Singapore Strait and ambient seas. Marked locations – 1: Pulau Iyu Kechil, 2: Horsburgh Lighthouse, 3: Tanjung Uban, 4: control point, 5: St. John's Island, 6: Pulau Lengkana, 7: Sembawang, 8: Jurong, 9: Pulau Sebarok, 10: Pulau Semakau, 11: Sungai Pulai, 12: Sungai Johor, 13: Pulau Bulan, 14: Pulau Kukup, 15: Pulau Karimun Besar.

### 2. BATHYMETRY AND BOUNDARIES

The currents and circulation in the seas around Singapore are strongly influenced by the bathymetry of the Singapore and Johor Straits and the proximity of the coastal boundaries (see Figure 1). On the northern boundary of the island of Singapore is the Johor Strait, which is divided into two parts by the causeway linking Singapore and Malaysia. Water depths in the Johor Strait range from a few m along the boundaries to about 10-20 m along the center of the straights. The width of the Johor Strait varies from about 0.5 to 2 km including the tidal flats on both sides of the strait. The main rivers flowing into the Johor Strait are Sungai Johor on the east and Sungai Pulai on the west. Both rivers are on the Malaysia side of the Johor Strait.

To the south of Singapore's coast is the Singapore Strait, bounded by Singapore's and Malaysia's southern coasts on one side and the northern coasts of Indonesia's Riau Islands on the other. The Singapore Strait connects the Malacca Strait on the west to the South China Sea on the east. The Malacca and Singapore Straits are connected to the Java Sea through Selat Durian, Selat Combol, Selat Riau and several other minor straits between islands. The narrowest part of the Singapore Strait is about 5 km and between Singapore and Pulau Batam, the range is about 5 km to 15 km. From the southern end of the Malacca Strait to the South China Sea, the

water depths are generally less than 50 m. However, in a small area just off the coast to the south-east of St John's Island, water depths reach more than 100 m.

The Singapore Strait is influenced by the exchange of waters between the Indian Ocean, the Malacca Strait and the South China Sea. Water depths range from thousands of meters in the basin east of Vietnam, to hundreds of meters in the shelf, and tens of meters in Singapore and Malacca Straits. In the southern half of the Malacca Straits, the water depths are in the order of a few tens of meters. North of the Malacca Strait, the water depths deepen rapidly towards the Andaman Seas, down to a thousand meters.

## 3. DRIVING FORCES

Currents in South East Asian seas, covering the Malacca and Singapore Straits, Java seas and South China Sea are driven by the monsoon winds and tides and also boundary fluxes at the coastal and open boundaries of the domain. Although winddriven currents are dominant in the open areas, such as the South China Sea, the influence of the wind on the currents in the Singapore and Malacca Straits are less significant compared to the influence of tidal forcing. Most predictions of the hydrodynamics in the Singapore Strait based on tidal forcing at the boundaries compare well with measurements obtained in the Strait. Residual ocean currents associated with the monsoons occur, and they are an order of magnitude smaller than the peak tidal currents. River flows linked to the monsoon storms can be significant in the near field of the rivers. However, their contributions to the currents in the Singapore Strait are relatively insignificant compared to the peak tidal currents.

Tides in the both the Malacca and Singapore Straits are semi-diurnal. The overall circulation is driven mainly by the combination of M2, S2, K1, O1, N2 and K2 tides, of which the M2 tide is the most dominant component. Being at the node between the Malacca Strait and the South China Sea, the tidal dynamics in the Singapore Strait is complex. In a joint study on tides and currents in the Malacca and Singapore Straits (JTCS, 1979), it was noted that the dominant M2 tides generated in the South China Sea and the North Indian Ocean interacted in the Singapore Strait. The tidal range varies from about 2.8 m in the west of Singapore to about 1.5 m to the east of Singapore (MPA, 2000).

#### 4. TIDAL CURRENTS

With the advent of computational capabilities in the past two decades, several attempts have been made to model the hydrodynamics in the Singapore Strait and the surrounding waters. Some of the recent efforts include boundary fitted grid models and full three dimensional models (e.g. Shankar et al., 1997; Chen et al., 1997; Zhang and Gin, 2000; Pang and Tkalich, 2003). The predictions typically compare well with the limited measurements available for validations, especially in the comparison of tidal levels. The prediction accuracy of the finer features of the tidal flows is dependent on the numerical model, the baseline information, and the



(c) 10.5 hours after the reference time

(d) 14 hours after the reference time



(e) 19.5 hours after the reference time

(f) 22.5 hours after the reference time

Figure 2. Snapshots of typical tidal currents in the Singapore Strait and ambient seas associated with Northeast Monsoon Spring tides (see Figure 3 for time reference).

prescribed boundary conditions. Typically the boundary conditions are based on tidal elevations at the boundaries of the Singapore Straits, either derived from the results of the joint study of the Malacca and Singapore Straits (JTCS, 1979), or from tidal harmonics predictions Total Tide (2002). Recent modeling efforts are beginning to rely on boundary conditions prescribed further away from the Singapore Strait domain in order to minimize the influence of boundary inaccuracies.

Figures 2a to 2f depict typical snapshots of depth averaged currents associated with the Northeast Monsoon spring tidal cycles. These snapshots were derived using a semi-implicit sigma-coordinate hydrodynamic model developed at the Tropical Marine Science Institute, National University of Singapore (Pang and Tkalich, 2004).

For these simulations, tidal elevations were prescribed at the boundaries of the computational domain far away from the boundaries of the Singapore Strait. Tidal elevations at Horsburgh Lighthouse, Tanjung Uban and a control point within the Singapore Strait (Figure 1) are shown in Figure 3.

The computation was conducted in 2-D mode with a horizontal grid size of 100 by 100 m. The model was validated with available measurements at selected locations. Figure 4 shows the comparison of predicted and measured currents at the control point off the east coast of Singapore in the Singapore Strait (Figure 1).

Currents, in general, are typically less than 2 m s<sup>-1</sup> in most parts of the Singapore Strait except in the narrow channel between St John's Island and Pulau Lengkana (Figure 1). Easterly flows in the Singapore Strait are usually associated with a rising tide and remain eastward flowing when the tidal elevation in the strait dips slightly before rising again (compare Figures 2a-f with Figure 3). On the other hand,



Figure 3. Tidal elevations at Horsburgh Lighthouse, Tanjung Uban and a control point within the Singapore Strait (see Figure 1 for locations).



Figure 4. Comparison of computed and measured currents at the control point in Singapore Strait (see Figure 1 for the location).

westward flows in the Singapore Strait are associated with decreasing tides. When currents are streaming from the Horsburgh Lighthouse (Figure 1) towards the west (Figures 2a-d), the tidal streams first bend towards the south through the straits connecting the Malacca and Singapore Straits to the Java Sea (Figure 1). After the first peak flow, the currents will weaken (Figure 2b), sometimes even flowing weakly towards the east (MPA, 2003), after which the westerly flow will strengthen again but with the flows on the west heading northwest through the Malacca Strait (Figures 2c and d). During this time, the currents through Selat Durian, Selat Combol and Selat Riau also head northward to join the westward going flows in the Singapore Strait. The westward flows in the Singapore Strait will subsequently

weaken and turn eastward while the flows in the Malacca Strait, Selat Durian, Selat Combol and Selat Riau Straits are still northward. During the eastward flow, a prominent eddy is also evident on the north eastern side of St John's Island. At the next turn of the flow direction in the Singapore Strait, the flows in the other straits also weaken and reverse in direction, leading back to the scenario shown in Figure 2a.



*Figure 5.* Envelopes of velocity vectors over a typical 15 days Northeast monsoon period. The arrows represent the net currents.

The above snapshots are typical of the spring tide cycles and demonstrate the complex interactions of tides in the Singapore Strait and ambient seas. While the flow directions associated with maximum flows are streamlined, those associated with the weaker flows are more complex. To illustrate the flow characteristics in the Singapore Strait, envelopes of hourly velocity vectors over a 15 days Northeast Monsoon period were obtained at selected locations and presented in Figure 5. Also included are the vectors representing the mean speed and direction over the same period.

A flatter envelope suggests a flow that switches between two dominant directions like oscillatory flows in a narrow wave flume. A more rounded envelope suggests the rotation of flow directions during the tidal excursion. The flatter envelope between the east coast of Singapore and Pulau Batam is consistent with the predominant east-west flows in this domain. A similar bi-directional scenario is evident at locations in the southern end of the Malacca Straits between Pulau Kukup (Malaysia) and Pulau Karimun Besar (Sumatra). The domain between the south west

coast of Singapore, Pulau Karimun Besar and Pulau Bulan (west of Pualu Batam) yields a much more complex flow scenario due to the change in flow directions in the Malacca Strait, Selat Durian and the Singapore Strait.

The net currents during the Northeast monsoon are westward in the Singapore Strait and northwards in the Malacca Strait (Figure 5). These net directions are reversed during the Southwest monsoon.

## 5. IMPLICATIONS ON TRANSPORT PROCESSES

In the Singapore Strait and ambient seas, particulates and dissolved matter in the water column are advected and dispersed mainly by the tidal currents. Occasional strong winds and waves would enhance the mixing in the upper layers. In terms of the suspended solids, the water column is not always well mixed. Vertical profiles of physical and biological parameters could be well structured depending on the tidal conditions, the river discharges, and also the surface winds and waves.

Considering the typical tidal flow characteristics (Figures 2a-f and Figure 5), some basic features of the transport processes could be identified. Given the dominant east-west streaming in the eastern part of the Singapore Strait, any matter discharged into the eastern Singapore Strait can be expected to oscillate east and west according to the tidal advection, with spreading mainly in the same directions.

Once the advected volume moves past the constriction of St John's Island towards the west, the advection could head southward or northward. When the tidal flow reverses, some of the transported matter would be transported back eastward following the tidal streams. During the Northeast Monsoon period, the mean drift is towards the Malacca Strait (Figure 5). During the Southwest monsoon, the mean drift is towards the South China Sea. Animation 1 depicts the transport of waterborne particles discharged at a location off the east coast of Singapore. The process of dispersion, oscillatory advection and mean drifts is evident in the animation. It should be noted that the dispersion of the particles also means a reduction in the concentration and hence a dilution of the source concentration. The streaming of the tidal flows (Figures 2a-f) also suggest that discharges at the southern end of Malacca Strait, Selat Riau, Selat Combol or Selat Durian may enter the Singapore Strait domain depending on the monsoon period and the phasing of the discharge relative to the tidal phases.

The hydrodynamic processes discussed above are important in determining the mixing and transport of anthropogenic inputs. The impact of these inputs on the environment, however, is also dependent on the coupling of these processes with the biological and chemical kinetics, especially in the cases of oil pollution and ballast water discharges.



Animation 1. Depth-averaged velocity field and transport of matter originally discharged in Singapore Strait during the Northeast monsoon spring tide. 1000 particles were introduced at the source point. The subsequent particle locations were derived using a particle tracking model with dispersion physics incorporated. The animation depicts the transport process up to 80 hrs after release.

### 6. CASE EXAMPLE: OIL SPILL

Oil spilled in the marine environment can pose a significant threat to marine life. The water-soluble components of crude oils and refined products include a variety of compounds that are toxic to a wide spectrum of marine plants and animals. Aromatic compounds are generally more toxic than aliphatics, and middle molecular weight constituents are generally more toxic than high molecular weight tars (Doerffer, 1992). A spillage of diesel fuel with a high aromatic content, is therefore much more damaging than bunker fuel oil and weathered oil, which generally have lower aromatic contents. The ecological effects of oil pollution depend on the type and amount of oil, the frequency of exposure, light and heavy oil fractions, environmental conditions (water temperature, salinity, nutrient concentrations, tide movements, wind, currents), the use of chemical dispersants and their associated toxicity and the sensitivity of specific local biological communities to the toxic effects of hydrocarbons (Price et al., 1999). Some petroleum hydrocarbons (e.g.

polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs)) have the capacity to concentrate in the tissues of marine organisms, with concentration increasing up the food chain (Baker, 1983). The result is that toxic levels could be reached for organisms at the end of the food chain, including birds and humans.

The collision between two large oil tankers, the *Evoikos* and *Orapin Global*, on 15 October, 1997, was the catalyst for recent oil spill research in Singapore, ranging from bioremediation studies, oil spill model development to environmental impact assessment. To date, this is the largest oil spill in Singapore (MPA Annual Report, 1997), with the amount discharged (28,500 tonnes) accounting for more than one third of the total oil lost for the total oil lost at sea for the world in 1997 (ITOPF, 1998). The collision occurred at night off Pulau Sebarok (Figure 1) in the Singapore Strait during spring tides. Within a few days after the collision, the oil slick had landed on the intertidal coastlines of several southern islands in the Singapore Strait. Some of the immediate questions following the spill included 1) what were the short and long-term impacts on marine life? and 2) how long would the effects of the spill remain in the marine environment?

In terms of assessing impacts on marine organisms, an understanding of baseline conditions prior to the spill was required, which, unfortunately, was unavailable at the time. Nevertheless, field monitoring studies were carried out to provide a partial biological assessment of the aftermath of the *Evoikos* oil spill and clean-up efforts conducted subsequent to the spillage (Tan et al., 1999). In general, the oil spill did not cause a major ecological disaster involving seawall molluscan communities and corals, the major organisms monitored in the study. However, both species abundance and species diversity of molluscs fluctuated considerably at both impacted and control sites. Thus, this factor needs to be taken into consideration in future studies so that a more robust dataset can be established. In addition, it is clear that biological baseline data is necessary so that impacts from future oil spills can be properly evaluated.

## 6.1. An oil spill-food chain model

While direct measurements of marine organisms can be used for impact assessment of oil spills, there is often a need to go beyond current situations, and to predict future scenarios. This is where models can be used to assist port managers in dealing with accidental oil spills. For example, one important application of oil spill modeling is to predict where the oil slick is likely to travel, whether it will encounter sensitive marine areas, and what time frame is involved? This will then allow port managers to allocate emergency clean-up measures to the right places and hopefully, avoid excessive ecological damage.

An oil spill-food chain interaction model for coastal waters was developed to assess the probable impacts of oil spills on several key marine organisms (Gin et al., 2001). The model consists of two parts: i) a multiphase oil spill model (MOSM) which combines sub-modules for oil slick dynamics at the water surface, oil sedimentation near the seabed and transport of the oil phases in the water column (Tkalich et al., 2003) and ii) a pelagic food chain model (Chapra, 1997) which considers the interactions between oil uptake and phytoplankton, zooplankton, small

fish, large fish and benthic invertebrates. MOSM is able to compute the concentrations of specific organic compounds in their dissolved and particulate phases both in the water column and benthic layer. It provides the mass exchange between the media and oil phases, as well as losses due to evaporation, hydrolysis, photolysis, oxidation and biodegradation using a kinetic approach. Transport of the oil components and phases in the water column are simulated using the velocities and diffusivity pre-computed with a 3-dimensional hydrodynamic model.

In the food-chain model, phytoplankton, zooplankton, small fish and large fish are assumed to uptake dissolved oil from all layers of the water column, while benthic invertebrates uptake dissolved oil from the layer of water adjacent to the bed sediments as well as from within the bed sediments (Huda, 1999; Gin et al., 2001). Zooplankton and benthic invertebrates are the predators of phytoplankton; small fish are the predators of both zooplankton and benthic invertebrates; and large fish are the predators of small fish. The uptake rates for the model were estimated using the mathematical formulation suggested by Connolly (1991) while the toxicant transfer efficiencies across the organism membrane and assimilation efficiencies, which are related to the octanol-water partition coefficient ( $K_{ow}$ ), were estimated from Thomann and Muller (1987). In the specific case of the *Evoikos-Orapin Global* oil spill, anthracene was chosen as the target compound of interest as it formed the major component for this particular spill. Using a hypothetical accidental spill of 28,000 tonnes, the fate and transport of the spilled was computed for typical hydrodynamic scenarios (e.g. Figure 6).



Figure 6. Surface slick thickness and oil droplet concentrations at 3 m depth.

The results of the simulation also showed that the concentrations of anthracene in the phytoplankton, zooplankton, small fish, large fish and benthic invertebrates one day after the spill were below the lethal toxicity levels ( $LC_{50}$ ). Field measurements of polycyclic aromatic hydrocarbons (PAHs) in benthic invertebrates (i.e. the gastropod mollusc, *S. guamensis*) at different places in the Singapore Strait after the *Evoikos-Orapin Global* oil spill ranged between  $9.5 \times 10^{-5}$  to  $1.0 \times 10^{-3}$  g kg<sup>-1</sup>. The results simulated from the oil spill-food chain model gave corresponding anthracene concentrations ranging from  $1 \times 10^{-4}$  to  $5 \times 10^{-3}$  g kg<sup>-1</sup>, which is within the range observed for the field measurements. The model was not verified for other marine organisms due to the lack of field data.

#### 6.2. Bioremediation studies

In the longer term, oil spilled in the marine environment will most likely undergo biodegradation by microorganisms. In the specific case of the *Evoikos* oil spill, most of the accumulated oil on the beaches and breakwaters were cleaned-up manually, with the aid of chemical dispersants. However, for the more inaccessible beaches and cleaned beaches with residual oil, biodegradation is most likely the main mechanism for oil removal. In these cases, the rate at which biodegradation of oil-based compounds can proceed is often limited by the lack of nutrients, particularly nitrogen and phosphorus. Numerous field and laboratory tests worldwide have shown that overcoming these limitations results in the successful enhancement of oil biodegradation (Bragg et al., 1994). Hence, a bioremediation study was conducted to investigate whether the indigenous microbial populations could be stimulated by the addition of nutrients (Mathew et al., 1999).

Two control plots and two treated plots measuring 1 m by 0.5 m were established on the isolated beaches of Pulau Semakau, an island 15 km south of Singapore (Figure 1). The four plots were constructed using corrugated steel sheets fixed to a depth of 0.25 m in the sand and to a height of 0.5 m and spaced 5 m apart. All four plots were located so that they would be subject to diurnal tidal flooding. 100 kg of beach sediment contaminated with oil from the *Evoikos-Orapin Global* oil spill was added to each plot. A mixture of 0.4 kg ammonium nitrate (NH<sub>4</sub>NO<sub>3</sub>) and 0.5 kg potassium hydrogen phosphate (K<sub>2</sub>HPO<sub>4</sub>) was dissolved in seawater and added to two of the experimental plots, while the remaining two plots were left untreated to act as controls. Sampling (from all four plots) and nutrient addition to the two treated plots were carried out five times over a period of 50 days. However, storm damage to the plots prevented extended sampling. The field samples were analyzed for (a) biological activity using the dehydrogenase enzyme assay; (b) total heterotrophic plate counts and (c) total petroleum hydrocarbons (TRPH) using standard methods.

The results clearly showed that the plots augmented with nutrients had significant reductions in TRPH (using the two sample *T*-test as a confidence interval of 95%) compared to the controls, especially towards the end of the experimental period (Table 1). This was supported by the enhanced activity of indigenous microbes (using the dehydrogenase enzyme assay) (Table 2) as well as increase in heterotrophic bacteria concentrations measured for the treated plots. Thus, the

404

addition of nitrogen and phosphorus had a clear stimulatory effect on indigenous microbial populations. These microbes had an innate ability to degrade hydrocarbons under suitable environmental conditions, presumably as a result of adaptation/ acclimatization to intermittent exposure of petroleum hydrocarbons from oil spillages in the Singapore Strait over time. This study has demonstrated that nutrient addition is able to significantly accelerate the natural degradation process. Given the warm temperatures in Singapore, biodegradation rates and hence, oil contaminant removal, can be expected to be high as long as nutrient augmentation is carried out.

 Table 1. Average (n=3) Total Recoverable Petroleum Hydrocarbons (TRPH) data from reference (A&C) and nutrient amended (B&D) plots (expressed as percentages of dry weight of the sediment).

Day	Reference	Amended	Reference	Amended
	Plot A	Plot B	Plot C	Plot D
0	6.72	6.98	6.97	6.97
7	6.38	6.59	6.59	6.72
15	6.21	6.55	6.54	5.33
25	6.40	6.29	6.28	4.52
49	6.77	6.40	6.40	3.87

**Table 2.** Average (n=3) dehydrogenase activity data from the reference (A&C) and nutrient amended (B&D) plots (expressed as  $\mu g$  INTF (iodonitrotetrazolium formazan) formed / g dry weight of the sediment  $h^{-1}$ ).

Day	Reference	Amended	Reference	Amended
	Plot A	Plot B	Plot C	Plot D
0	11.47	11.46	12.02	10.26
7	5.19	11.94	5.47	11.97
15	4.08	13.05	4.00	8.99
25	4.72	11.98	3.21	7.56
49	6.34	12.28	6.00	7.66

#### 6.3. Persistent organic pollutants in Singapore's marine environment

While most organic compounds are largely biodegradable, there are some chemicals which remain highly recalcitrant to chemical and biological degradation, and therefore persist in the environment for long periods. These Persistent Organic Pollutants (POPs) include the organochlorine pesticides (OCPs), polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs). POPs are known to adversely affect the endocrine system in both wild fauna and humans, have a propensity to bioaccumulate in the lipid fraction of biological tissues and are subject to biomagnification in both terrestrial and aquatic food webs. Humans may be chronically exposed to environmental (POPs) via the ingestion and inhalation pathways (Duarte-Davidson and Jones, 1994), and many such compounds have been

detected in a range of human tissues including serum, breast milk and adipose tissue (Dewailly et al., 1993). In 2001, many countries signed the Stockholm Convention under the United Nations Environment Programme to implement measures to reduce and eliminate the release of POPs into the environment, including bans on production, import, export, and use of certain POPs (UNEP, 2001). For Singapore, with the combination of a heavy shipping traffic and numerous ship building yards, petroleum refineries, and pharmaceutical manufacturing plants located along the coastline, it is important to track and prevent both operational and fugitive discharges of POPs. Data on the prevalence of POPs to the marine ecosystem and human health. Since 2001, a study has been initiated to capture data on the prevalence of POPS in Singapore's coastal marine environment.

Marine water samples within 1 km of the coastline of Singapore were analysed to determine prevalent concentrations of a range of POPs by Basheer et al. (2003). Samples were collected from 0.5 m and mid-depth at twenty-two locations. The POPs analysed were classed as USEPA priority pollutants, and included: sixteen polycyclic aromatic hydrocarbons (PAHs); eight polychlorinated biphenyls (PCBs); and twelve organochlorine pesticides (OCPs) (Table 3).

Polycyclic Aromatic	Organochlorine	Polychlorinated Biphenyls
Hydrocarbons (PAHs)	Pesticides (OCPs)	(PCBs)
Naphthalene	α-BHC	2-chlorobiphenyl
Acenaphthylene	Lindane	2,3-dichlorobiphenyl
Acenaphthene	β-ΒΗC	2,4,5-trichlorobiphenyl
-		2,2',4,4'-
Fluorene	Heptachlor	tetrachlorobiphenyl
	-	2,2',3',4,6-
Phenanthrene	Aldrin	pentachlorbiphenyl
		2,2',4,4',5,6'-
Anthracene	Dieldrin	hexachlorobiphenyl
		2,2',3,3',4,4',6-
Fluoranthene	Endrin	heptachlorobiphenyl
		2,2',3,3',4,5',6,6'-
Pyrene	Endosulfan II	octachlorobiphenyl
Benz[a] anthracene	p,p'-DDD	
Chrysene	p,p'-DDT	
Benzo[a] fluoranthene	Endrin aldehyde	
Benzo[k] fluoranthene	Methoxychlor	
Benzo[a]pyrene	,	
Indeno[1,2,3-cd]pyrene		
Dibenz[a,h] anthacene		
Benzo[ghi]perylene		

 
 Table 3. Types of Persistent Organic Pollutants (POPs) analysed in the survey of northeastern and southwestern sectors of Singapore coastal waters.

406

#### 6.3.1 Polycyclic aromatic hydrocarbons

All sixteen PAHs were detected in all water samples from both depths at every sample location. Total PAH concentrations in seawater ranged from 93.0 to 1419.6 ng  $l^{-1}$  and from 88.4 to 1472.8 ng  $l^{-1}$  in the northeastern and southwestern region, respectively. The overall mean total PAH concentrations for seawater depth levels were as follows: surface, 235.1 $\pm$ 46.2 ng l<sup>-1</sup>; and mid-depth, 343.1  $\pm$ 61.5 ng l<sup>-1</sup>. The highest total PAH concentrations measured were obtained at locations off Sembawang (in the northeastern sector) and off Jurong (Figure 1) (in the southwestern sector), which are both in the vicinity of shipyards and industrialized coastal areas. The lowest concentrations of total PAHs for these regions were obtained at locations remote from industrial areas and where the water column was well mixed by strong currents. Among the sixteen PAHs measured, the highest individual PAH concentrations measured were for six ring indeno[1,2,3-cd]pyrene i.e. 712.9 ng  $l^{-1}$  and 218.8 ng  $l^{-1}$  at the northeastern and southwestern regions, respectively. The lowest concentrations of acenapthylene detected were 1.3 ng l<sup>-1</sup> and 1.9 ng  $1^{-1}$ , respectively. This distribution profile may reflect the different properties of low and high molecular weight PAHs, where low molecular weight compounds have higher vapour pressure and water solubility, and are therefore more readily volatilized and degraded by microbial activity. In contrast, higher molecular weight PAHs are more likely to be associated with the particulate phase within the water column and undergo sedimentation, thereby accounting for their higher concentration at mid-depth. Similar vertical distributions have been previously noted in a study of Baltic coastal waters by Broman et al. (1991). At mid-depth, PAHs were dominated by indeno[1,2,3-cd]pyrene, but other abundant compounds included dibenzo[ah]anthracene, benzo[ghi]perylene and anthracene.

Overall, higher molecular PAH compounds were more prevalent in Singapore coastal waters than lower molecular weight compounds. The prevailing ocean currents in the region most likely govern the fate of PAHs, and the presence of localized high levels of PAHs may be a function of petroleum discharges from shipping. The highest total PAH concentration detected in Singapore's coastal waters (i.e. 1472.8 ng  $\Gamma^1$ ) is greater than that reported for Xiamen Harbour, China i.e. up to 945 ng  $\Gamma^1$  (Zhou et al., 2000); the German-Baltic sea i.e. 6.7 ng  $\Gamma^1$  (Witt, 1995); the Coral Sea, Australia i.e. 240 ng  $\Gamma^1$  (Smith et al., 1987); Chesapeake Bay, USA i.e. 14.05 ng  $\Gamma^1$  (Ko and Baker, 1995); the Northwestern Black Sea, Ukraine i.e. 0.7 ng  $\Gamma^1$  (Maldonado et al., 1999); and Admiralty Bay, Antarctica i.e. 80 ng  $\Gamma^1$  (Bicego et al., 1996), but lower than concentrations reported for Rhode Island, USA i.e. 115,000 ng  $\Gamma^1$  during an oil spill event (Reddy and Quinn, 1999).

## 6.3.2. Organochlorine pesticides (OCPs)

In Singapore, extensive agricultural activities have been phased out for more than two decades. Although some minimal agricultural activities remain, they do not generally involve extensive use of the types of pesticides discussed in the present work. However they are used in neighbouring countries. Nevertheless, OCPs were detected in samples taken at both depths from all locations from both the northeastern and southwestern region.

Total OCP concentrations ranged from 4.0 to 22.0 ng  $l^{-1}$  and 3.0 to 21.9 ng  $l^{-1}$  at the northeastern and southwestern regions, respectively. Overall, higher concentrations were detected in the northeastern region, which is most likely due to the confined waters in the northeast, which limits the hydrodynamic dispersion of contaminants. This river runs across agricultural, commercial and industrial land in Malaysia and into the Straits of Johor, adjacent to Singapore. BHC and Dieldrin were the most abundant pesticides present and their levels ranged from 0.13 to 17.87 ng  $l^{-1}$ , and 0.34 to 6.91 ng  $l^{-1}$  and in northeastern and southwestern regions respectively. In both regions, the highest concentration Lindane, 0.34 ng  $l^{-1}$ ; Endrin, 1.97 ng  $l^{-1}$ ; p,p'-DDT, 1.14 ng  $l^{-1}$ ; and p,p'-DDD, 1.17 ng  $l^{-1}$  at northeastern and southwestern locations respectively.

OCPs are, to a variable extent, insoluble in seawater (< 1 ppb), but are readily soluble in fat and adsorb strongly onto suspended particulates in the water column. The surface layer of the sea comprises a film of about 1 mm of thickness, which is known to contain fatty acids. Due to the lipophilic and persistent nature of OCP, accumulation in this surface layer is known to occur (Zhou and Rowland, 1997). OCP enrichment of the surface film may be of considerable importance to surface living organisms or to birds that skim food off the sea surface. Surface plankton and other organic particulates are readily associated with OCPs and undergo subsequent sedimentation. In general, higher amounts of OCPs were detected at mid-depth locations close to industries and shipping anchorages, where hydrodynamic dispersion is confined.

The land area under agriculture use in Singapore is negligible and there is no direct application of organochlorine pesticides in the country. However, pesticides may be easily transported through the ambient environment by different mechanisms including volatilization from soil and spray drift during application to crops (Dörfler and Scheunert, 1997). The presence of OCPs in Singapore's marine waters is probably a function of their use in neighbouring countries.

Concentrations of OCPs measured in Singapore seawater are comparatively lower than those detected in water from the Selangor River in Malaysia; i.e. Aldrin, up to 884.00 ng  $\Gamma^1$ ; Dieldrin, up to 850.00 ng  $\Gamma^1$ ; Endrin, up to 10970.0 ng  $\Gamma^1$ ;  $\alpha$ -Endosulfan, up to 8.90;  $\beta$ -Endosulfan, up to 12270 ng  $\Gamma^1$ ; Heptachlor, up to 13710.00 ng  $\Gamma^1$ ; Lindane, up to 40950.0 ng  $\Gamma^1$ ; p,p'-DDT, up to 44770.00 ng  $\Gamma^1$ ; p,p'-DDE up to 2310.00 ng  $\Gamma^1$  (Mustafa et al., 2000); as well as the Surabaya river, Indonesia p,p'-DDT up to 49.63 ng  $\Gamma^1$  (Dewi, 2000); Philippine coastal waters,  $\alpha$ -BHC up to 21 ng  $\Gamma^1$  and aldrin at 7 ng  $\Gamma^1$  of (Santiago, 2000); the Dampha and Balat estuaries in Vietnam, DDT i.e. 30.00 ng  $\Gamma^1$  (Viet et al., 2000); Bohai Sea, China, DDE, DDD and DDT up to 50 ng  $\Gamma^1$  (Yeru and Hao, 2000). However, OCP levels in Singapore's coastal waters are higher than those found in the Coral Sea, Australia where total OCP concentrations have been measured at 1.21 ng  $\Gamma^1$  (Tanabe et al., 1984), and 5.5 ng  $\Gamma^1$  (Kurtz and Atlas, 1990).

#### 6.3.3. Polychlorinated biphenyls (PCBs)

PCBs represent a group of compounds that have been widely used in a range of industrial applications. All eight PCBs analysed in the study were detected in both the northeastern and southwestern sectors for the majority of sample stations.

Total PCB concentrations in seawater from both regions varied from 0.04 to 61.7 ng  $l^{-1}$  and 0.22 to 20.1 ng  $l^{-1}$  in northeastern and southwestern regions, respectively. The highest measured concentration of an individual PCB congener i.e. 2,2,'3,3',4,5',6,6'-octachlorobiphenyl was 40.71 ng  $l^{-1}$  and 15.42 ng  $l^{-1}$  at the northeastern and southwestern regions, respectively.

Long-range atmospheric transport is likely to be a source of PCBs detected in remote waters and results in low-level concentrations in nearly all environmental matrices (Bidleman et al., 1989). However, higher levels can be associated with proximity to industry, as well as waste discharges from shipbuilding yards and municipal sewage plants located in coastal regions. PCBs are hydrophobic compounds with an octanol-water partition coefficient ( $K_{ow}$ ) ranging from 4.5 to 8.2. The aqueous solubility is less than 5 mg l<sup>-1</sup> for the more chlorinated congeners (i.e. >2 chloro group) (Patil, 1991). The distribution of PCBs in coastal waters contrasts with that of PAHs, where the surface was more contaminated than at mid-depth for the majority of sample locations. The measurement of PCBs in seawater samples shows that the northeastern coastal region of Singapore has much higher concentrations than the southwestern region. These variations are most likely due to historic and episodic inputs from industrial sources as well as hydrodynamic factors.

The maximum level of PCB contamination detected in Singapore coastal waters (i.e. 61.7 ng  $\Gamma^{-1}$ ) is lower than that recorded from Xiamen, China and Victoria Harbour, Hong Kong i.e. 151 ng  $\Gamma^{-1}$  (Hong et al., 1995); Jamaica-Kingston Harbour, i.e.3,500 ng  $\Gamma^{-1}$  (Mansing et al., 1995); Doñana National Park, Spain i.e. 237 ng  $\Gamma^{-1}$  (Fernàndez et al., 1992); and higher than levels measured in the Gulf of Mexico and Atlantic Ocean (North) i.e. <0.003 ng  $\Gamma^{-1}$ , (Sauer et al., 1989), the Northern Pacific Ocean i.e. 0.59 ng  $\Gamma^{-1}$  (Tanabe et al., 1984) and the Dutch Wadden Sea i.e. 0.62 ng  $\Gamma^{-1}$  (Duinker and Hillerbrand, 1983).

## 7. CONCLUSIONS

The physical oceanography of the Singapore Strait and ambient seas is governed mainly by the tides together with a seasonal net circulation. The interaction of tidal streams from the Malacca Strait, South China Sea and straits linking the Malacca and Singapore Straits to the Java Sea makes the overall flow in the Singapore Strait rather complex. Being a node at the confluence of these interacting water bodies, any discharges in the domain, such as oil spills, would affect the surrounding seas, although the concentration would be diluted through mixing and transport. In addition to physical processes, the ultimate fate of a pollution event would depend on the coupled interactions with biology and chemistry of the water body, including food-chain interactions and biodegradation. For the more persistent organics in the marine environment, baseline studies showed that concentrations of PAHs measured in Singapore's coastal waters were generally higher than levels reported elsewhere, whereas OCPs and PCBS were generally lower than reported levels for other Asian countries, but higher than some levels reported elsewhere in the world. Overall, the prevalence of POPs in Singapore's coastal waters suggest the need for continued monitoring and evaluation of their transport and biological impact in the marine environment.

#### 8. ACKNOWLEDGEMENTS

This study was supported by the Agency for Science & Technology, Singapore (ASTAR), the Tropical Marine Science Institute and the Maritime & Port Authority of Singapore. The assistance of Mr. Pavlo Zemskyy in the preparation of this chapter is appreciated.

#### 9. REFERENCES

- Baker, J.M., 1983. Impact of oil pollution on living resources, Commission on Ecology Papers 4, IUCN, Gland, Switzerland. 218-230.
- Basheer, C., Lee H. K., Obbard, J.P., 2003. Persistent Organic Pollutants in Singapore's Coastal Marine Environment, Part I: Seawater. Water, Air & Soil Pollution149, 295-313.
- Bícego, M. C., Weber, R. R., Goncalves Ito, R., 1996. Aromatic hydrocarbons on surface waters of admiralty bay, King George Island, Antarctica. Marine Pollution Bulletin 32, 549-553.
- Bidleman, T. F., Patton, G. W., Walla, M. D., Hargrave, B. T, Vass, W. P., Erickson, P., Flower, B. Scott, V.,Gregor, J., 1989. Texaphene and other organochlorine in Arctic Ocean fauna: evidence for atmospheric delivery. Arctic 42, 307-313.
- Bragg, J.R., Prince, R.C., Harner, E.J., Atlas, R.M., 1994. Effectiveness of bioremediation for the Exxon Valdez oil spill. Nature 368, 413-418.
- Broman, D., Näf, C., Rolff, C., Zebűr, Y., 1991. Occurrence and dynamics of polychlorinated dibenzo-pdioxins and dibenzofurans and polycyclic aromatic hydrocarbons in the mixed surface layer of remote coastal and offshore waters of the Baltic. Environmental Science and Technology 25, 1850-1864.
- Chapra, S.C., 1997. Surface Water Quality Modeling. McGraw Hill, New York, USA, 784 pp
- Chen, M., Khoo, B.C., Chan, E.S., 1997. Three dimensional circulation model of Singapore's coastal waters. Proceedings of *Oceanology International 97 Pacific Rim 1*, 12-14 May, Singapore.
- Connolly, J.P., 1991. Application of a food chain model to polychlorinated biphenyl contamination of the lobster and winter flounder food chains in New Bedford Harbor, Environmental Science and Technology, 25, 760-770.
- Dewailly, E. Ayotte, P. Bruneau, S. Laliberte, C. Muir, D.C.G., Norstrom, R., 1993. Inuit exposure to organochlorines through the aquatic food chain in Arctic Quebec. Environmental Health Perspectives 101, 618-620.
- Dewi, R., 2000, Environmental Monitoring on Endocrine-Disrupting Chemicals (EDCs) in Indonesia, The UNU International Symposium on Endocrine Disrupting Chemicals (EDCs), Environmental Governance and Analytical Techniques - EDCs in East Asian Coastal Hydrosphere. University of Malaya, Kuala Lumpur, Malaysia.
- Doerffer, J.W., 1992. Oil Spill Response in the Marine Environment. BPCC Wheatons Ltd, Great Britain, U.K., 125 pp.
- Dörfler, U., Scheunert, I., 1997. S-Triazine herbicides in rainwater with special reference to the situation in Germany. Chemosphere 35, 77-85.
- Duarte-Davidson, R., Jones, K.C., 1994. Polychlorinated biphenyls (PCBs) in the UK population: estimated intake, exposure and body burden Science of the Total Environment 151, 131-153.
- Duinker, J. C., Hillebrand, M. T. J., 1983. Comparison of PCBs mixture in biotic and abiotic marine compartments (Dutch Wadden Sea). Bulletin Environmental Contamination and Toxicology 31, 25-32.

410

- Fernàndez, M. A., Fernàndez, M., Gonzalez, J., Tebera, M. C., 1992. Organochlorine compounds and selected metals in waters and soils from Doñana National Park (Spain). Water, Air and Soil Pollution 65, 293-305.
- Gin, K.Y.H., Huda, M.K., Lim, W.K., Tkalich, P., 2001. An oil spill-food chain interaction model for coastal waters. Marine Pollution Bulletin 42, 590-597.
- Hong, H., Xu, L., Zang, L., Chen, J.C., Wong, Y.S., Wan T.S.M., 1995. Environmental chemistry fate and chemistry of organic pollutants in the sediments of Xiamen and Victoria harbors. Marine Pollution Bulletin 31, 229-236.
- Huda, M.K., 1999. Development of a multiphase oil spill model for environmental impact assessment. M.Eng. thesis, National University of Singapore, Singapore.
- ITOPF, 1998. The International Tanker Owners Pollution Federation Ltd. Statistics. (http://www.itopf.com/stats.html).
- JTCS, 1979. Report on the joint tidal and current studies in the straits of Malacca and Singapore. Indonesia, Japan, Malaysia, Singapore.
- Ko, F.C., Baker, J.E., 1995. Partitioning of hydrophobic organic contaminants to resuspended sediments and plankton in the mesohaline Chesapeake Bay. Environmental Science and Technology49, 171-188.
- Kurtz, D.A., Atlas, E.L., 1990. Distribution of hexachlorocyclohexanes in the Pacific Ocean basin, air, water, 1987, In: Kurtz, D.A. (Eds.), Long range Transport of Pesticides. Lewis Publishers, MI, USA, pp. 143-160.
- Mansing, A., Wilson, A., 1995. Insecticide Contamination of Jamaican Environment III. Baseline Studies on the Status of Insecticidal Pollution of Kingston Harbour. Marine Pollution Bulletin 30, 640-645.
- Maldonado C., Boyona, J. M., Bodineau, L., 1999. Sources, distribution, and water column processes of aliphatic and polycyclic aromatic hydrocarbons in the Northwestern Black Sea water. *Environmental Science and Technology* 33, 2693-2702.
- Mathew, M., Obbard, J.P., Ting, Y.P., Gin, K.Y.H., Tan, H.M., 1999. Bioremediation of oil contaminated beach sediments using indigenous microorganisms in Singapore. Acta Biotechnology 19, 225-233.
- MPA, 1998. The Making of an International Maritime Centre Seeing the Big Picture, Annual Report 1997, Maritime and Port Authority of Singapore, pp.64.
- MPA, 2003. Charts for small craft. Singapore Strait & Adjacent Waterways, Maritime and Port Authority of Singapore, Singapore.
- Mustafa, A.M., Melissa, C., Pui, L., Cheng, L., Abdul Rani, A., 2000. Pesticide residues in water from the Selangor River, Malaysia, The UNU International Symposium on Endocrine Disrupting Chemicals (EDCs). Environmental Governance and Analytical Techniques - EDCs in East Asian Coastal Hydrosphere. University of Malaya, Kuala Lumpur, Malaysia.
- Pang W.C., Tkalich P., 2003. Modeling tidal and monsoon driven currents in the Singapore Strait, Singapore Maritime & Port Journal, 2003, pp 151-162.
- Pang W.C., Tkalich P., 2004. Semi-Implicit Sigma-Coordinate Hydrodynamic Model. Proceedings 14th IAHR-APD Congress, Name and Location of Publisher ? Hong Kong.
- Patil, G.S., 1991. Correlation of aqueous solubility and octanol-water partition coefficient based on molecular structure. *Chemosphere* 2, 723-738.
- Price, J.M., Marshall, C.F., Lear, E.M., 1999. Supplement to oil spill risk analysis: Gulf of Mexico OCS central and western lease sales. Mineral Management Service, Environmental Division, Elden, Herndon, USA, pp.318-327.
- Reddy, C.M., Quinn, J.G., 1999. GC-MS analysis of total petroleum hydrocarbons and polycyclic aromatic hydrocarbons in seawater samples after the North Cape oil spill. Marine Pollution Bulletin 38, 126-135.
- Santiago, E. C., 2000. Monitoring of EDC in the East-Asian hydrosphere: Report from The Philippines, The UNU International Symposium on Endocrine Disrupting Chemicals (EDCs). Environmental Governance and Analytical Techniques - EDCs in East Asian Coastal Hydrosphere. University of Malaya, Kuala Lumpur, Malaysia.
- Sauer, T.C. Jr., Durell, G.S., Brown, J.S., Redford, D., Boehm, P.D., 1989. Concentration of chlorinated pesticides and PCBs in microlayer and seawater samples collected in the open ocean waters off the U.S. East Coast in the Gulf of Mexico. *Marine Chemistry* 27, 235-257.
- Shankar, N.J., Cheong, H.F., Chan, C.T., 1997. Boundary fitted grid models for tidal motions in Singapore coastal waters. Journal of Hydraulic Research 35, 47-60.

- Smith, J. D., Bagg, J., Sin, Y.O., 1987. Aromatic hydrocarbons in seawater, sediments and clams from Green Island, Great Barrier Reef, Australia. Australian Journal of Marine and Freshwater Research 38, 501-530.
- Tan, K.S., Johnson, B., Goh, B.P.L., Tun, K.P.P., Low, J.K.Y., Gin, K.Y.H., Ting, Y.P., Obbard, J., Tan, H.M., Mathew, M., Chou, L.M., 1999. An assessment of the impact of the Evoikos oil spill on the marine environment in Singapore, Singapore Maritime and Port Journal, 1999, 69–81.
- Tanabe, S. Tanaka, H., Tatsukawa, R., 1984. Polychlorobiphenyls, DDT, and Hexachlorocyclohexane isomers in the Western North Pacific ecosystem'. Archives of Environmental Contamination and Toxicology 13, 731-738.
- Thomann, R.V., Mueller, J.A., 1987. Principles of Surface Water Quality Modeling and Control. McGraw Hill, New York, USA, 549-576.
- Tkalich, P, Huda, M.K. and Gin, K.Y.H., 2003. A multiphase oil spill model. Journal of Hydraulic Research 41, 115-125.
- TotalTide, 2002. User Manual, United Kingdom Hydrographic Office. 2002 Edition.
- UNEP, 2001. Stockholm Convention on Persistent Organic Pollutants, United Nations Environmental Programme, Geneva, Switzerland.
- Viet, P. H., Hoai, P.M., Hung, P.T., Lieu, T. T., 2000. Persistent organochlorines in environment of coastal hydrosphere: A case study in Vietnam, The UNU International Symposium on Endocrine Disrupting Chemicals (EDCs). Environmental Governance and Analytical Techniques - EDCs in East Asian Coastal Hydrosphere. University of Malaya, Kuala Lumpur, Malaysia.
- Witt, G., 1995. Polycyclic Aromatic hydrocarbons in water and sediments of the Baltic Sea. Marine Pollution Bulletin 31, 237-248.
- Yeru, H., Hao, Q., 2000. Environmental monitoring and governance of Endocrine Disrupting Chemicals (EDCs) pollution in the East Asian coastal hydrosphere due to EDCs in water, The UNU International Symposium on Endocrine Disrupting Chemicals (EDCs). Environmental Governance and Analytical Techniques - EDCs in East Asian Coastal Hydrosphere. University of Malaya, Kuala Lumpur, Malaysia,.
- Zhang, Q.Y., Gin., K.Y.H., 2000. Three-dimensional numerical simulation for tidal motion in Singapore's coastal waters. Coastal Engineering, 39, 71-92.
- Zhou, J. L., Rowland, S.J., 1997. Evaluation of the interactions between hydrophobic organic pollutants and suspended particles in estuaries waters. Water Research 31, 1708-1718.
- Zhou, J. L., Hong, H., Zhang, Z., Maskaoui, K., Chen, W., 2000. Multi-phase distribution of organic micropollutants in Xiamen Harbour, China. Water Research 34, 2132–2150.