
Potential impacts of emissions from outboard motors on the aquatic environment: a literature review



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C. Depree

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National Institute of Water & Atmospheric Research Ltd
Gate 10, Silverdale Road, Hamilton
P O Box 11115, Hamilton, New Zealand
Phone +64-7-856 7026, Fax +64-7-856 0151
www.niwa.co.nz

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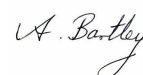
M. Stewart

Approved for release by:



R. Wilcock

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1. Scope

Recreational boating raises a number of issues for resource managers and the public, including noise complaints, safety concerns and environmental impacts. The potential impacts of recreational boating have been divided into the following areas (Rijkeboer et al. 2004).

- The impact on local air quality.
- The impact on local water quality, subdivided into:
 - As related to ecosystems (including sediments).
 - As related to the product of drinking water.
- The impacts of noise, subdivided into:
 - The impact of noise on ecosystems (i.e., birds and underwater wildlife).
 - The impact of noise on nuisance as perceived by humans.

This report is focussed on the potential impacts of boat derived contaminants on water quality – both environmental toxicity and drinking water criteria. Physical impacts on the aquatic environment from recreational boating activities (i.e., resuspension of sediments, bank erosion etc.), are not covered in this report.

2. Introduction

Over the last 30 years the use of motorised recreational craft on rivers, lakes and water storage reservoirs has increased significantly, which has led to concerns about the potential increasing environmental pressures being placed on these aquatic environments. The growth in recreational boating, is impart, being driven by advances in materials technology that have made water skiing and power boating equipment more affordable. Accordingly, high-speed power boating and personal water craft (jet ski's) activities have become more popular and accessible to a wider section of the community. This trend is reflected in Canada by an annual growth in power boat sales of 3% (Jaakson, 1993). In Australia, Mercer (1977) reported that power boating and water skiing activities were increasing at the rate of 20-24% per year. This general increase in activity, combined with perceptions of safety, ease of accessibility, and calmness of water, has lead to a large and increasing percentage of recreational boating taking place on inland water bodies. This, in turn, has resulted in an increasing demand by the public for the development of more reservoirs and lakes (Department of Community Service and Health, 1990).

With respect to total emissions, recreational water craft do not contribute significantly; for example, recreational boating emissions of non-methane hydrocarbons (NMHC) represent only 0.5% of the total emissions for the European Union (Rijkeboer et al. 2004). The contribution of atmospheric hydrocarbons from recreational boating to the national total in the US has been estimated at 1.59% (Hare and Springier, 1973). However, the high density and nature of boating emissions mean that there is scope for localised impacts on both air and water quality. Although not the subject of this report, briefly, the main concern about air pollution from recreational boating is the potential for localised high concentrations of smog forming components [nitrogen oxide gases (i.e., NO_x) and volatile organic compounds, or VOC], resulting in ground level ozone formation. This phenomenon may often be seen in some sheltered lakes and bays that receive heavy power boat use (Warrington, 1999). Ozone irritates the respiratory tract and eyes with exposure to high levels resulting in chest tightness, coughing and wheezing. People with respiratory and heart problems are at a higher risk, and ozone has been linked to increased hospital admissions and premature death. Furthermore, these emissions from boating activities may occur in otherwise pristine environments that are not impacted by non-point contaminant emissions associated with major urban centres.

With respect to water quality issues, the combination of the inefficient trapping efficiency (defined as the ratio of fuel trapped in the engine to that which is delivered to the engine) of 2-stroke engines and the release of exhaust emissions beneath the water surface, results in relatively large amounts of combustion products and unburned fuel being mixed into surface waters. For example, two stroke engines can

typically release 10-25% of their fuel (petrol/oil mixture) unburned into the waters (Warrington, 1999). The EPA has estimated that a single jet ski (or personal water craft, or PWC) can emit up to 23 litres of fuel in just two hours of operation (Blue Water Network, 1998). Accordingly, many regulatory agencies, particular in the state of California, have placed either bans or restrictions on the use of certain types of 2-stroke powered recreational boats, including PWC's on a number of lakes and reservoirs (Department of Boating and Waterways, 2007).

There are conflicting results from studies regarding the ecological and human risk posed by recreational boating, and this report aims to provide a balanced summary of the available literature relating to the potential risk of recreational boating activities to water quality. At the time of writing the report, there was no information available on boating numbers/density on West Coast lakes or the proportion of 2-stroke carburetted, 2-stroke direct injection and 4-stroke outboard engines. Therefore, the report is limited to merely describing literature studies; no attempt has been made to transfer for the finding of these international studies to a New Zealand or, more specifically, a West Coast context. This is an important point to stress, as the impacts of recreational boating on various environmental compartments including water, are site-, time- and use-specific – that is, general applicable statements will not be valid under all conditions (Warrington 1999).

3. 2-Stroke vs 4-stroke outboard engine emissions

In general, two-stroke engines emit ca. 10-times more pollution than 4-stroke engines because of lower trapping efficiencies inherent in the 2-cycle operation. Unlike 4-stroke engines that have separate exhaust and fuel filling cycles, in 2-stroke engines the exhaust and fuel filling occur in the same stroke, resulting in an un-preventable loss of unburned fuel in the exhaust. Depending on load and configuration, it has been reported that 2-stroke engines release 1-40% of their fuel unburned to the water. Warrington (1999) concluded that 10-25% was a more typical range for normal use of modern 2-stroke engines. Although the data is somewhat out-dated (1973), to give this a global perspective, Jackiviz and Kuzminski (1973) calculated that of the 3.8 billion litres of fuel used per year by outboard engines, 380-600 million litres are discharged (unburned) into the water.

US EPA standards have forced engine manufacturers to significantly reduce the emissions of 2-stroke engines, which has largely been accomplished by direct fuel injection technology (opposed to carburetion). Despite improvements (largely with respect to air quality emissions), these 2-stroke engines still release much higher quantities of contaminants than 4-stroke outboard engine of similar horsepower. Kado et al. (2000) compared particulate matter (PM) emissions from 2 types of 2-stroke engines [carburetted (C) and direct injection (DI)] and a 4-stroke (carburetted) engine. All the engines were 1998 or 1999 models and had a maximum power rating of 90 hp. The total PM emissions for the 67 min test procedure were <0.47 g (similar to background levels), 1.95g and 9.23 g for the 4-stroke, 2-stroke/DI and 2-stroke/C engines, respectively. The total amount of PM-bound PAHs released during the test period was <27 µg, 3600 µg, and 1900 µg for the 4-stroke, 2-stroke/DI and 2-stroke/C engines, respectively. Genotoxic activity (using *Salmonella*) of the 4-stroke PM was only 2-3% of the PM released from the 2-stroke engines. It is worth noting that the 2-stroke/DI engine used in the test meet the U.S. Federal and HC and NO_x emission standards for the year 2006. In another study, Jüttner et al. (1995) reported that for a 10 minute running period, a 10 hp 2-stroke engine introduces 23.8 g of benzene, toluene, ethyl-benzene and xylenes (BTEX chemicals) into the water, compared to only 0.5 g for an equivalent 4-stroke engine. The study also showed that 2-stroke emissions aged for up to 14 days were still more toxic than freshly contaminated water from a 4-stroke engine.

Despite the increased reliability, efficiency and ca. 10-fold lower emission levels of 4-stroke outboard engines, 2-stroke engines still dominate the market (Rijkeboer et al. 2004); however, a comparison of 1996 and 1999 sales figures for Europe show a steady increase in the market share of 4-stroke engines. For European Union countries with outboard sales of more than 10,000 units, the percentage of 4-stroke outboards ranged from ca. 20% (e.g., Norway and Spain) to greater 50-60% (UK and Finland). The increase in 4-stroke outboards sales is largely attributable to the lower power

range (4-16 hp), which are less significant contributors of emissions compared to higher power output engines. In the 150-200 hp range (European data), the percentage of 4-stroke engine sales for the years 1996-2000, 2001 and 2002 were 0, <1, and ca. 10% respectively (Rijkeboer et al. 2004). Although no outboard sales figures beyond 2002 were available, because of the inherently lower emission levels of 4-stroke engines, this is an important parameter for assessing any future impacts of emissions from recreational boating activities.

4. Chemical contaminants from outboard motors that are of concern

Recreational motorboats release a variety of contaminants to the air and water, which are summarised in Table 1. In addition to these, there is concern about metal contaminants originating from fuel additives used to improve the octane rating of fuels. While the lead additives, tetraethyl- (TEL) and tetramethyl-lead (TML) are no longer used, there are concerns regarding the use of the manganese fuel additive, methylcyclopentadienyl manganese carbonyl (MMT). MTBE is relevant to North American studies, however, its use in NZ is reportedly not very widespread (Ministry for Economic Development, 2001a). While particulate matter could possibly contribute to a reduction in water quality (i.e., in very pristine, oligotrophic lakes, the main contaminants of concern for water quality are BTEX, MTBE and PAHs).

Table 1: Contaminants released into the water by recreational power boats.

Acronym	Full name
BTEX	benzene, toluene, ethyl benzene and xylene
MTBE	methyl- <i>t</i> -butyl ether
PAHs	polycyclic aromatic hydrocarbons
CO	carbon monoxide
NO _x	nitrogen oxides
PM	particulate matter
SH	saturated hydrocarbons

4.1 BTEX

BTEX are monocyclic aromatic compounds that make up 20-50% of petrol. Depending on the fuel (regular or super), BTEX comprises ca. 25-35% of New Zealand petrol (Ministry for Economic Development, 2001b). Besides the aromatic content, petrol consists of C₄-C₁₂ aliphatic hydrocarbons, which can be broken down into 4-8% *n*-alkanes, 2-5% alkene, 25-40% *iso*-alkanes, 3-7% cycloalkanes and 1-4% cycloalkenes. Unlike PAHs, BTEX chemicals are all very volatile and are rapidly eliminated from the water by evaporative processes. The half-life of BTEX chemicals has been shown to be approximately 1 day – so even though the concentrations of BTEX chemicals can be high immediately after the passage of a boat, these levels rapidly decrease as a large portion is volatilized into the air (Correll, 1999; Bouchard, 2000-01). Despite BTEX chemicals being priority water contaminants, their very short residence times in the bulk water phase tend to keep BTEX field concentrations orders-of-magnitude below established toxicity thresholds (Commonwealth of Massachusetts, undated). A potential problem of BTEX chemicals, however, is their

ability to impart an unpleasant taste/odour on drinking water at very low concentrations (Section 9.1).

4.2 PAHs

Unburned petrol contains relatively small amounts of 2 and 3 ring methylated PAHs, including the methylated analogues of naphthalene, fluorene and phenanthrene. Incomplete combustion processes of the petrol generate higher molecular weight 4-7 ring PAHs. In general, PAHs with more than 3 rings have poor biodegradability and can accumulate (TRPA, 1999). The smaller 2-3 ring PAHs are generally more water soluble, more biodegradable and more volatile. Their solubility makes them more bioavailable (i.e., greater risk) to aquatic life, although this is off-set by their low persistence and hence reduced exposure durations. The larger 4-7 ring PAHs are much less water soluble and have a strong tendency to bind to sediment. Unlike the lower molecular weight PAHs, larger PAHs don't biodegrade readily (environmentally persistent) and tend to accumulate in sediments. Because of these properties, small PAHs are generally regarded as more of an immediate (acute) threat to organisms in the water column, while larger PAHs represent a more long-term (chronic) threat to sediment dwelling organisms (VanMouwerik and Hagemann, 1999). While most field studies have shown bulk water phase concentrations to be many times lower than ecological protection guideline values, there is a growing awareness about the impacts PAHs have in relation to the surface microlayer and enhanced photo-toxicity (Section 8).

4.3 MTBE

MTBE is widely used in the U.S., initially to boost the octane value of the fuel, and then in greater amounts (up to 15%) as an oxygenate to reduce tail pipe emissions. MTBE is reportedly not widely added to petrol in NZ, although current regulations allow levels up to 11%. Relative to BTEX and PAHs, which are relatively hydrophobic and have low water solubilities, MTBE is very soluble in water with ca. 46 g dissolving per litre of water (ca. 5% aqueous solubility) and it is resistant to biodegradation (Sakata, 2000-2001). Furthermore, it does not react to UV light (no photo-oxidation) and it rarely adsorbs to suspended particulate matter (Tahoe Research Group, 1997). MTBE from powerboat emissions do not represent any threat to human health because water concentrations of 151 mg/L are required to be acutely toxic, or 51 mg/L for chronic toxicity (US-EPA, 2006). To put this in perspective, MTBE concentrations at Lake Tahoe in the vicinity of boating activity were often in the range of 20-35 µg/L (Reuter et al. 1998), which is ca. 7500-times lower than the acute toxicity value. Adverse effects on rainbow trout are not expected until the concentrations of MTBE in the water column reach 4600 µg/L. MTBE water quality guidelines for the protection of fresh water and marine organism have been set at 3400

$\mu\text{g/L}$ and $440 \mu\text{g/L}$, respectively (Environmental Protection Division, 2001). However, like BTEX, MTBE can impart detectable taste and odour on potable water at concentration as low as $20\text{-}40 \mu\text{g/L}$ (Section 9.2). Based on odour/taste threshold levels, the EPA has set a guideline value for MTBE of $20 \mu\text{g/L}$, and the State of California has set a primary drinking water standard for MTBE of $13 \mu\text{g/L}$, and a secondary drinking water standard of $5 \mu\text{g/L}$ (California Environmental Protection Agency, 1999). Concentrations of MTBE in surface waters of reservoirs with intensive levels of recreational power boating can routinely exceed $5 \mu\text{g/L}$. This is a major concern for many regulatory agencies, especially since current water treatment technology is ineffective at removing the trace levels of MTBE.

Several U.S. studies have indicated a correlation between BTEX, MTBE and PAHs concentration measured in the field and recreational power boat usage. The concentrations often increase throughout the summer boating season (May to September; northern hemisphere), with distinct spikes occurring after peak boating dates on public holidays (Allen et al. 1998; Allen and Reuter, 1999; Miller and Fiore, 1997; Oris et al. 1998; Reuter et al. 1998b). These levels of contaminants tend to diminish within weeks or months of the boating season finishing (returning to almost background levels), and therefore do not appear to significantly degrade the overall water quality (Warrington, 1999; Revelt 1994). However, as BTEX, MTBE and PAHs have been shown to exhibit acute toxicity to a number of aquatic organisms, there is concern about the impact of even short term exposure of organism to outboard emissions during periods of high boating activity.

5. Toxicity of outboard exhaust emissions

Outboard emissions have been shown in a number of studies to be toxic to aquatic organisms under either laboratory conditions or mesocosm experiments employing unrealistically high concentrations of outboard exhaust concentrations or individual contaminant concentrations. The vast majority of field investigations have concluded that normal levels of recreational power boating are not having a long-term negative impact on water or sediment quality in lakes. The basis of these findings has come from the observation that field concentrations of contaminants in sediments and the bulk water column are many times lower than reported ecological guidelines. Many of these guideline values are based on toxicity to adult stage organisms, and do not take into account for more sensitive life stages of organisms. Consequently, there is now growing evidence that field concentrations during periods of high boating activity on small lakes (with limited capacity for dilution) could result in PAH concentrations high enough to inhibit early life stage development of some fish (Koehler and Hardy, 1999). Oris et al. (1998) has actually reported that PAHs levels present in Lake Tahoe arising from 'ambient levels of motorised water craft emissions are present at sufficiently high concentrations to cause measurable adverse impacts on fish larval growth and zoo plankton survival/reproduction as a result of enhanced phototoxicity of PAHs (Section 8). Concern regarding the sensitivity of juvenile life stages to contaminants is further increased by the potential for order-of-magnitude higher contaminant concentrations in the surface microlayer – the upper 30-50 μm . This surface microlayer is an area of high biological production and is a nursery for many organisms (egg and larval life stages), and hence the combination of contaminant enrichment in the surface microlayer (Section 7) and phototoxicity (Section 8) has the potential for significant adverse effects.

A summary of the relevant literature describing the potential toxicity of outboard engine exhaust and its individual aromatic components is given below.

Swedish workers assumed a water exhaust concentration of 0.7 mg/L of hydrocarbons based on exhaust emission being confined to a 1 metre path behind the boat. Using this and higher concentrations of fuel placed into water, toxicity experiments were conducted by extracting the exhaust components from the water and injecting into fish. A number of toxicological responses were noted including enzymatic, reproductive and genetic effects. The applicability of these results to real field situations is questionable as realistic exhaust concentrations and uptake of hydrocarbons by the fish would be significantly lower than the body burdens used in the experiments (Tjarlund et al. 1995). Furthermore, the exposure of the fish to the exhaust plume may only be for a very short time; that is, it is unlikely that fish would swim behind the boat being constantly exposed to the maximum concentration of exhaust contaminants.

The goldfish, *Carrasius auratus*, was subject to a dynamic bioassay using a continuous flow of outboard exhaust condensate and aromatic compounds (Warrington, 1999). The LC₅₀'s (concentration result in 50% mortality over the duration of the experiment) for exhaust components ranged from 172 mg/L (96 hour test) to 226 mg/L (24 hour test) of fuel burned. Assuming 25% of the fuel delivered to the engine was released unburned; this corresponded to 43-57 mg/L of exhaust pollutants in water. The 24 hour LC₅₀'s for the aromatic compounds toluene and xylene were determined as 41.6 and 30.6 mg/L (the respective 96 hour LC₅₀'s were 22.8 and 16.9mg/L).

English et al. (1963) reported relatively high tolerances (LC₅₀, 96 hour test) of the test sunfish, *Lepomis macrochirus*, and *Pomoxis annularis*, to outboard exhaust emissions of 526 mg/L, based on fuel delivered to the engine. Alaskan freshwater fish species exposed to benzene exhibited 96 hour LC₅₀ concentrations ranging from 11.7 to 14.7 mg/L (Moles et al. 1979). It should be noted that these values exceed the aromatic levels found in the Boating Industry Association (BIA)/Environmental Control Technology Corporation (ECTC) tests ponds, stressed with very high inputs of outboard exhaust emissions (3-times that possible for recreational boating), by a factor of 100-1000. Since fish kills did not occur in the BIA/ECTC test ponds it is reasonable to assume that for the species and life stages of fish studied, outboard exhaust emissions are not acutely toxic under normal boating conditions.

The sub-lethal biological effects of outboard engine exhaust emissions on fish remain poorly studied. In contrast, many studies have focussed on the effects of crude oil and petroleum, and since these contain many of the main components of outboard engine exhaust, the results may be comparable. The first sign of sub-lethal effects are manifested at behavioural changes, then, with increasing hydrocarbon concentrations, physiological effects become apparent. Sub-lethal concentrations of petroleum hydrocarbons have been observed to effect swimming performance, equilibrium and spontaneous activity patterns. Although such behavioural effects can be observed, it is often difficult to determine their significance with respect to long-term survival of the organism. Physiological effects of exposure to petroleum hydrocarbons include changes in growth, heart rate, respiratory rate, alterations in embryonic activity, premature or delayed hatching and malformed larvae. It is the changes affecting reproductive success that are most damaging and hence of greatest concern. Malins and Hodgins (1981) reviewed several studies which reported decreased larval survival and gross morphological abnormalities after hydrocarbon exposure in the low mg/L to high µg/L range. There is now considerable evidence indicating that relatively low concentrations of petroleum hydrocarbons are toxic to fish eggs and larvae, and that these life stages are at greatest risk from outboard engine exhaust emission to receiving waters.

Carls et al. (1999) reported that total PAH concentrations of 0.7 µg/L (from weathered crude oil) caused malformations, genetic damage, mortality, decreased size and inhibited swimming in Pacific herring eggs. Concentrations of 0.4 µg/L resulted in sub-lethal responses including yolk sac edema and immaturity consistent with premature hatching. Studies with Pink salmon embryos led Heintz et al. (1999) to conclude that water quality standards for total PAHs above 1.0 µg/L may fail to protect fish embryos. The authors recommended a protection standard of 0.01 µg/L (or 0.01 ppb) for total PAHs in water, which includes a safety factor of ca. 100.

Outboard exhaust emissions have been shown to be toxic to benthic macro-invertebrates. The 24 hr LC₅₀ concentration of outboard exhaust for amphipods (*Gammarus fasciatus*) and snails (*Amnicola limnosa*) was 1.16 and 1.08 mg /L, respectively. The authors reported that no toxic effects were apparent in the field.

Microalgal (phytoplankton) productivity in BIA/ECTC test ponds (mesocosm) subject to high levels of outboard exhaust emissions was significantly lower than that of microalgae in control ponds. This was further supported by a study by the Rensselaer Institute that found when raw fuel levels in the water exceeded 3 to 5 mg/L, the C¹⁴ uptake by indigenous Lake George algae was inhibited. The hydrocarbons in the exhaust emissions were found to be more inhibitory to carbon fixation than raw fuel (Hilmer and Bate, 1982).

While phytoplankton productivity can be adversely affected by hydrocarbon levels associated with heavy boating use, it is important to note that the BIA/ECTC test ponds (referred to above) received a stressing level three times the maximum outboard engine usage which could be sustained on a given surface area of water. Furthermore, studies reporting a decrease in photosynthetic rates used an exhaust concentration that was 390-times higher than that typically expected from normal boating usage. Under conditions of normal outboard engine use, exhaust emissions were not found to inhibit the growth of the algal species, *Selenastrum capricornutum* and *Anabaena flos-aquae* (Kuzminski and Fredette, 1976; Chmura and Ross, 1978).

The lack of adverse impacts in the field from bulk water concentration of outboard exhaust contaminants is not surprising when considering the concentrations of aromatic hydrocarbons reportedly toxic to various organisms are typically >1 mg/L; with the exception of some larvae where toxicity is reported at 0.1 mg/L (US EPA, 1985). Jüttner reported LC₅₀ concentrations of aromatic compounds for *Daphnia* of 14-237 mg/L and 0.2-6.9 mg/L for the bacteria, *Vibrio fischeri*. The higher sensitivity of bacteria highlights the importance of considering the potential impacts of high contaminant levels in the surface microlayer, which is enriched in micro-organisms. Mesocosm experiments using BIA/ECTC ponds receiving 3-times the exhaust emissions possible under saturation boating conditions maximum yielded a maximum aromatic hydrocarbon concentration of 1.0 mg/L. This level returned to <0.1 mg/L

within 2 days of ceasing engine activity. In contrast, equivalent mesocosm experiments in Michigan test ponds resulted in maximum aromatic hydrocarbon concentrations of just 0.01-0.05 mg/L, with no significant difference between the exhaust-treated and control ponds. The difference between the two sites was attributable to the rapid elimination of aromatic hydrocarbons by a combination of evaporation, adsorption or biodegradation (BIA, 1975).

6. Environmental fate of outboard emissions

All modern outboard engines exhaust below the water surface (mostly through the propeller hub), and as a result, all emissions pass through the water. A significant proportion of the emissions remain in the gas phase and is released directly to the atmosphere. The remainder condenses and is mixed into the water column and, depending on their physical properties, becomes suspended in the water column or forms a film on the surface for varying lengths of time. The condensed emissions are eventually eliminated from the water by a combination of physical, chemical and biological processes.

Outboard engines are highly conducive to dispersing engine exhaust in the water, with the propeller turbulence and boat movement through the water resulting in significant dilution. Hare and Springier (1973) showed that the percent removal of hydrocarbons from the water was more rapid in experiments with the propeller on because of increased mixing/aeration. In addition they showed that hydrocarbon removal was also greater with high water to exhaust ratios, which explains why laboratory studies often underestimate the elimination rate of hydrocarbons from the water column. A considerable amount of research by US agencies has been directed at characterising and quantifying outboard engine emissions to the aquatic environment (Hare and Springier, 1973; BIA, 1975). European investigators (Warrington, 1999) have also reported on outboard emissions in Austria, Germany, Norway, and for the Bodensee, a lake bordering Switzerland, Austria and Germany.

Exhaust emissions contain gases (water vapour, oxygen, carbon dioxide, carbon monoxide, nitrogen oxides and hydrocarbons), which rapidly rise through the water column as bubbles, and condensable components which can be transferred to the water column. The condensable components consists of unburned fuel, combustion derived PAHs, fuel additives (e.g., MTBE is present) and partially oxidised hydrocarbons (e.g., phenols and carbonyl compounds).

The organic composition of the gas phase exhaust hydrocarbons is similar to that of the fuel. Warrington (1999) reanalysed data reported by Hare and Springier (1973), and estimated that ca. 60% (range 30-75%) of the exhaust hydrocarbons escape directly to the atmosphere as exhaust gas bubbles. Thus ca. 40% of the emitted hydrocarbons are temporarily retained in the bulk water phase. Compared to the fuel, the aromatic fraction of the condensed hydrocarbons is enriched in two ring aromatics molecules (i.e., naphthalene) and contains higher molecular weight, combustion derived, PAHs.

6.1 Evaporation

Of the ca. 40% of hydrocarbons that are temporarily retained in the bulk water phase, it has been estimated that at least 90% of outboard hydrocarbon emissions move to the surface as a film. Experiments conducted using tracer dyes injected into an outboard engine exhaust showed that emissions were dispersed in two tracks, each about 3 m wide and 4 m from the centreline of the boat's wake (IMEC, 1979). The tendency of condensed hydrocarbon to rapidly migrate to the surface explains why bulk water phase concentrations of exhaust contaminants in the field, and mesocosm ponds, are generally very low.

The rapid migration to the surface means that evaporation at the air-water interface is the major removal mechanism for hydrocarbons. Once at the surface, evaporation of volatile hydrocarbons is very rapid because of the large surface area-to-volume ratio of the hydrocarbon film. Calculations by Warrington (1999) have shown that volatile fuel components evaporate as fast as they reach the surface of the water. For example, a boat with a 200 hp 2-stroke engine travelling at 70 km/h can be expected to emit 13.5 kg of unburned fuel to the water per hour. Assuming the gasoline is deposited of an 8 metre wide strip, the theoretical maximum area of deposition will be 560,000 m². Using a water temperature of 10 °C and wind speed of 10 km/h, the calculated time for evaporation is only 0.13 seconds. This is much quicker than observed elimination rates of hydrocarbons from the bulk water phase, implying that the rate limiting step in the loss of fuel hydrocarbons from water appears to be the mixing of exhaust products and their subsequent rise or diffusion to the surface, not the evaporation rate at the surface. Correll (1999) reported that if BTEX compounds are mixed below 1m, the rate of evaporation slows and is a function of the rate of mixing in the water column.

A BIA/ECTC tank study found that the evaporative half-life for volatile aromatic hydrocarbons dispersed to a depth of 1 m under aerated conditions (i.e., prop turbulence) was ca. 1 day. In the field, however, the much lower fuel-to-water ratio, larger surface area for film formation, increased turbulence, wind and lower initial concentrations, results in much shorter half-lives Warrington (1999). Shuster et al. (1974) found that, on average, 65% of the exhaust products were removed in under 1.5 hours at water temperature between 10°C and 30°C.

While most of the volatile gasoline hydrocarbons evaporate quickly, there is a non-volatile hydrocarbon fraction in exhaust emissions which remains to interact with the aquatic environment by other mechanisms. Volatile hydrocarbons are generally considered those that contain less than 11 carbon atoms (Rijkeboer et al. 2004). Because petrol is comprised of largely of C₄-C₁₂ aliphatic compounds and C₆-C₈ mono-aromatic compounds (i.e., BTEX), the vast majority of unburned hydrocarbons are removed from the bulk water phase by evaporative processes. However, larger hydrocarbons, including 4-7 ring combustion derived PAHs and fuel additives such as

MTBE are not readily transferred to the air by evaporation (VanMouwerik and Hagemann, 1999). For these components, other elimination processes such as photo-oxidation, biodegradation, flushing and sedimentation may become more important.

6.2 Flushing

Flushing rates for boating situations can vary tremendously – from lakes with little outflow to large rivers. From an assessment of boating areas in British Columbia (Canada), Warrington (1999) concluded that flushing had little effect on contaminant removal compared to other processes such as evaporation and biodegradation.

6.3 Photo-oxidation

Photo-oxidation results in the preferential degradation of aromatic compounds (due to their ability to absorb light) and the process is enhanced by thin films and a high ionic content in the water (U.S.B., 1982). Most researchers have concluded that photo-oxidative degradation is likely to require days or weeks to be completed and that biodegradation would be initiated well before photo-oxidative removal.

6.4 Biodegradation

There are over 200 species of bacteria, yeast and filamentous fungi that are known to metabolize hydrocarbons. The rate of degradation depends on water temperature, the extent of hydrocarbon dispersion and the availability of nitrogen, phosphorus and oxygen. While a considerable amount of research has been carried out on the biodegradation of crude oil, relatively few studies have specifically looked at the biodegradation of outboard engine exhaust emissions. Shuster (1971) reported that microbes showed better growth rates on outboard exhaust products than on raw fuel. The Rensselaer Institute noticed accelerated activity in sediment microbes after a weekend of heavy boating. It was postulated that this stimulation was a result of the introduction of a carbon source (i.e., the exhaust components) to a carbon limited system (Shuster et al. 1974).

6.5 Sedimentation

Hydrophobic contaminants mixed into the water column will readily adsorb to particulate matter and re-suspended sediments, facilitating transport to the lake bottom and incorporation into sediments. High molecular weight combustion-derived PAHs are very persistent in the environment (i.e., slow biodegradation) and have the potential to accumulate in the sediment. The resuspension of sediment by recreational motorboats (and jet skis) operating in shallow water is, therefore, of concern as it provides a mechanism for sediment incorporation of contaminants. The maximum

water depth for sediment disturbance is dependent on engine power, but a 50 hp outboard motor is capable of disturbing sediments at a water depth of 3m (Warrington 1999). Laboratory experiments by the Rensselaer Institute indicated that re-suspended lake sediments were capable of adsorbing outboard engine exhaust products and carrying them to the bottom (Shuster et al. 1974). Some researchers consider the accumulation of combustion derived PAHs in sediments of lakes and reservoirs to be a more serious, but currently less understood, risk to aquatic life than water quality impacts from recreational boating (VanMouwerik and Hagemann, 1999).

In spite of this, the rate at which hydrocarbons reach the sediments appears to be quite slow. Only low levels of petroleum-derived hydrocarbons were detected in the sediments of certain bays of Lake George in New York – a lake that has received heavy outboard use over several decades (Shuster et al. 1974). Edwards (2002) measured sediment PAH levels in the Mary River flood plain billabongs (which receive extensive recreational boating activity in the dry season) but found all of the PAHs were below the detection limit of 10 ng/g. For 3-6 ring PAHs, the ANZECC (2000) low threshold values (a level below which there is a high probability of no toxic effect) for PAH are in the range 63-665 ng/g. The ANZECC high values (levels above which there is a high probability of pronounced effect on sediment dwelling organisms) for the same set of PAHs are in the range 540-2800 ng/g. Based on these guideline values, the authors had to conclude that there was no toxic effect from the current levels of recreational boating activities. A 3 year study on two lakes in Grand Teton National Park (Wyoming) found maximum sediment concentrations of phenanthrene and benzo[a]pyrene of 28 ng/g and 7.6 ng/g, respectively (Rhea et al. 2005). The respective ANZECC low thresholds for phenanthrene and benzo[a]pyrene of 240 ng/g and 430 ng/g suggest that even these ‘hot spot’ sediment concentrations pose no significant risk to sediment dwelling organisms. The BIA/ECTC test pond study was unable to find any statistically significant build up of hydrocarbons in test pond sediments after three years of heavy outboard engine operation that corresponded to 3-times the maximum possible recreational boating density. The absence of significant hydrocarbons in the sediments is evidence of the efficiency of the other degradation processes. Warrington (1999) postulated that it might also indicate that turbulence and the thermocline may act to keep the hydrocarbon-containing particulate matter in the upper layers where conditions for oxidation and biodegradation are optimal.

6.6 Summary: environmental fate

Condensed hydrocarbons do not accumulate in the bulk water column but are largely eliminated by a variety of naturally occurring mechanisms such as evaporation, biodegradation, dispersion and photo-oxidation. Certain contaminants, such as combustion-derived PAHs, tend to concentrate in the surface microlayer at toxic levels. Aromatic hydrocarbons remain in the water column for less than a day under

normal boating conditions and no enrichment of saturated hydrocarbons is observed even under very heavy boating levels. Accordingly, Cole (1974) concluded that under normal use levels there is no significant water quality degradation caused by outboard motors in large lakes of reasonable depth (e.g., surface area of 250 ha and a mean depth of at least 6 meters).

7. Surface microlayer

Unlike MTBE, which because of its high water solubility is dispersed more uniformly throughout the bulk surface water, the concentration of hydrophobic exhaust contaminants (i.e., hydrocarbons) is generally very low. As mentioned earlier, this is because the hydrocarbon components (BTEX and PAHs) rapidly rise to the surface to form a film near the water surface. While BTEX chemicals and some lower molecular weight PAHs are rapidly volatilised, the concentration of higher molecular weight (i.e., 4-7 ring) PAHs in the surface microlayer (30-50 μm depth) can be present at concentrations ca. 100-1000 times higher than in the underlying water column. For example, Moore and Freyman (2001) reported microlayer and underlying water concentrations of chrysene of 19.3 $\mu\text{g/L}$ and 0.02 $\mu\text{g/L}$, respectively from samples taken from Burrard Inlet (Vancouver). The authors reported microlayer contaminant enrichment factors of 100-10,000, and that the tidal action can coat intertidal organisms with these high levels of microlayer contaminants. While the subject of this report is inland water bodies, wind and/or boat generated waves and/or hydroelectric variation in lake level could have a similar effect on lake shoreline biota. Although contaminant enrichment in the surface microlayer is different from a visible hydrocarbon film on the water, Hammitt and Cole (1987) have stated that the deposition of thin films of unburned fuel on aquatic organisms (i.e., unicellular plankton and algae) is the 'primary ecological effect' of the operation of outboard motors. The effects of such films include interference with respiration and the inhibition of algal growth; ultimately affecting the food chains of fish and other aquatic organisms Hammitt and Cole (1987).

Contaminant enrichment in the microlayer is potentially significant because this layer is a nursery for many organisms, and is an area of very high production (i.e., plankton, microalgae, bacteria etc.). A number of studies have shown that juvenile life stages of many organisms are more sensitive to contaminants, such as PAHs, than adult life stages. For example, the 1999 interim Canadian water quality guidelines for the protection of aquatic life for benzo[a]pyrene (BaP) is 0.015 $\mu\text{g/L}$. Moore and Freyman (2001) reported BaP concentrations of up to 3.87 $\mu\text{g/L}$ (260 times higher than guideline value), highlighting the potential for adverse biological effects. However, it should be noted that this study did not involve waters impacted by recreational boating.

Clearly, there is a need for further research to characterise the concentration, residence times and biological effects of the surface microlayer in waters impacted by recreational power boating. This is especially important for PAHs because of their potential for enhanced phototoxicity which can increase toxicity by orders-of-magnitude (Section 9).

8. Phototoxicity of PAHs

Much of the PAH toxicity data from the literature that resource managers compare field data with do not take into account phototoxicity (Landrum et al. 1987; Mekenyan et al. 1994; Arfsten et al. 1996). Giesy (1997) reported that the toxicity of some PAHs found in two-stroke exhaust are as much 50,000 time more toxic in field conditions (exposed to UV light) than in laboratory tests (no UV light exposure). Accordingly, the phototoxic effect is very important to consider when determining acceptable levels of PAHs in the water that will not adversely impact on aquatic life. A study by Oris et al. (1998) found that ambient levels of PAHs in 2-stroke motorboat emissions had significant negative impacts on fish growth and zooplankton survival/reproduction in Lake Tahoe (US). Lake PAH levels ranged from 0.005-0.070 µg/L, but with enhanced phototoxicity, the no-observed-effect-concentrations (NOEC) for these PAHs were calculated as 0.009 µg/L for fish (fathead minnow), 0.007 µg/L for zooplankton (*Ceriodaphnia dubia*) survival, and 0.003 µg/L for zooplankton reproduction. The authors commented that in very clear oligotrophic lakes, the enhanced phototoxic impact of field PAH concentrations could extend to depths of 20 metres.

The study by Oris et al. is a rare example where biological impacts have been reported at field concentrations arising from recreational boating emissions, and highlights the importance of taking into account the phototoxic properties of PAHs. Based on these results, field concentrations of PAHs in the surface microlayer are presumably very toxic to resident plankton, eggs and juvenile life stages of various aquatic organisms. However, the nature of recreational boating usage means that high activity only occurs on fine weathered weekends and public holidays during the summer months. This sporadic activity possibly provides lakes with sufficient time to 'recover' from any temporary and relatively short-lived impacts that may arise from motorised recreational boating activity.

9. Drinking water impacts

9.1 Hydrocarbons

While field concentrations of outboard-derived contaminants are orders-of-magnitude lower than establish guideline values for the protection of aquatic life, components of 2-stroke engine exhaust can taint drinking water supplies at parts-per-billion concentrations. Jüttner et al. (1995) reported that running a 20 hp engine for 1 hour can impart an objectionable odour to 11,000 m³ of water (the equivalent of one Olympic-size swimming pool), which was largely attributed to the presence of aromatic compounds (i.e., BTEX and low molecular weight PAHs). Odour threshold concentrations of aromatic compounds commonly found in 2-stroke exhaust include, benzene (10 µg/g), toluene (1.0 µg/g), ethylbenzene (0.1 µg/g), *p*-xylene (0.53 µg/g), naphthalene (0.005 µg/g or 5 ng/g) and 1-methylnaphthalene (0.02 µg/g or 20 ng/g) (Van Gemert and Nettenbreijer, 1977). Kuzminski et al. (1974) similarly reported that low concentrations (ca. 0.3 µg/L, or 1 L of fuel per 3,000,000 L of water) of 2-stroke engine exhaust impart an unpleasant taste/odour on a drinking water. These findings were consistent with those of English et al. (1963) who reported that for every litre of fuel delivered to the engine, 0.6-1.3 million litres of dilution water are required for odour control.

The occasional occurrence of high density motorised boating in the proximity of water intakes may allow insufficient time (for evaporation) and/or dilution, resulting in seasonal or occasional complaints of objectionable, petroleum-based odours and tastes from outboard exhausts (Jackivicz and Kuzminski, 1973). Conventional water treatment appears to reduce but not eliminate odour problems. To prevent odour and taste problems in drinking water, it has been recommended that motorised watercraft (in particular those powered by 2-stroke engines) be banned from operating on water bodies used for drinking water supplies (Ludemann, 1968). However, Warrington (1999) recommended that motorised watercraft only need to be excluded from the immediate vicinity (within about 100 m but site specific) of water supply intakes and from small lakes (flushing rates longer than 1 year) that serve as domestic water supplies.

9.2 MTBE

MTBE has an odour threshold concentration of 20-40 µg/L, which prompted the EPA to implement a water quality guideline value for MTBE of 20 µg/L. Unlike hydrocarbons, MTBE is potentially more problematic on account of its relatively high solubility and much slower evaporation rates. Unlike BTEX compounds and other volatile hydrocarbons that have residence times measured in days, the half-life for MTBE has been estimated at 80-120 days (Reuter, 2007). The tendency of MTBE to

disperse throughout the water column has been demonstrated by Boughton and Lico (1997) who detected MTBE at depths of up to 30 m in Lake Tahoe during the boating season. Field sampling at Lake Shasta and Lake Perris in California have revealed MTBE concentrations in excess of the 20 µg/L EPA health advisory limit (Miller and Fiore, 1998; Clementsen, 1997; Dale et al. 1997). The banning of 2-stroke engines on Lake Tahoe and Lower Echo Lake resulted in a ca. 90% reduction in MTBE concentrations (Poppoff, 2000). As with hydrocarbons, because concentrations are highest in areas of high boating activity, power boats should not be allowed within 100 m of any drinking water intake in order to circumvent any potential problems with tainting domestic water supplies.

10. Summary

Normal levels of motorised recreational boating activity do not have a significant impact on water quality with respect to toxicity. The main contaminants of concern are BTEX compounds, PAHs and the fuel additive MTBE. The relevance of MTBE to NZ waters is unclear because although it is not widely used, currently regulations permit up to 11% of MTBE in petrol. The concentration of all these contaminant classes in the bulk water phase are generally orders-of-magnitude lower than establish water quality guidelines for the protection of aquatic life. However, an important caveat is that these guidelines do not always protect the most sensitive life-cycle stages of organisms (i.e., eggs/larvae) and certainly do not take into account for phototoxicity – for PAHs this can increase toxicity 50,000 fold. The majority of BTEX compounds and other volatile hydrocarbons are released directly to the atmosphere as rising bubbles of exhaust gases – the remaining volatile compounds that condense into the water are eliminated via evaporative processes. The rate limiting step in these processes is the migration of the contaminants to the surface-water interface – the evaporative process for most components (including BTEX chemicals) is very fast. High molecular weight PAHs also migrate to the surface of the water, but their reduced volatility can result in up to 1000-fold higher concentrations in the surface microlayer (30-50 μm depth). Accordingly, recreational boating activities may be negatively impacting on plankton production and the environmental compartment where eggs accumulate and larvae feed – this microlayer is thought to be crucial to the reproduction of many species. Even if such impacts do occur, it is important to establish the long-term impacts, as lakes typically have long recovery times between seasons of ‘high’ recreational boating activities.

In contrast to hydrocarbon contaminants, MTBE has relatively high water solubility and therefore can disperse throughout the water column. The tendency not to accumulate at the surface greatly reduces the evaporative elimination (the major pathway) of MTBE from the water.

Although outboard exhaust contaminants are not present in concentrations that exceed aquatic protection guidelines, there is a significant risk of boating activities tainting drink water (odour/taste). BTEX chemicals, low molecular aromatics and MTBE are capable of tainting water at concentrations as low as ca. 20 ng/L (ppb). Accordingly, it has been recommended that boating activities not be permitted within 100 m of a water intake structures or on small lakes (with slow flushing times) used for domestic water supply.

Despite the potential for negative impacts, it is important to emphasise that 4-stroke outboard emissions are at least 10-fold lower than those from the same powered 2-stroke engine. Trends in overseas outboard sales (latest data was 2002) show that 4-

stroke outboards are starting to dominate the small outboard engine market and from 2000-2002, the proportion of high-powered 4-stroke engine sales went from 0% to 10% of the market (European data). Hence it is important to ascertain how these trends have continued through to 2007, and if these suggest a general replacement of 2-stroke outboards by 4-stroke engines then this will have a large effect in the assessment of potential future (long-term) environmental impacts of motorised recreational boating activities. Moreover, much of the literature relates to lakes and reservoirs that sustain intense levels of motorised boating activity, if the situation on the West Coast of NZ involves large lakes with very low levels of boating activity then this also needs to be factored into any risk assessment. Finally, one major concern in the US is the rapidly growing number of personal water craft (jet skis etc.). These are a rapidly growing market that release disproportionately large amounts of fuel emissions into the water, and because they are jet powered, can access shallow waters that otherwise would not be disturbed by other forms of boating.

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