Effects of acidification on olfactory-mediated behaviour in freshwater and marine ecosystems: a synthesis

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For many aquatic organisms, olfactory-mediated behaviour is essential to the maintenance of numerous fitness-enhancing activities, including foraging, reproduction and predator avoidance. Studies in both freshwater and marine ecosystems have demonstrated significant impacts of anthropogenic acidification on olfactory abilities of fish and macroinvertebrates, leading to impaired behavioural responses, with potentially far-reaching consequences to population dynamics and community structure. Whereas the ecological impacts of impaired olfactory-mediated behaviour may be similar between freshwater and marine ecosystems, the underlying mechanisms are quite distinct. In acidified freshwater, molecular change to chemical cues along with reduced olfaction sensitivity appear to be the primary causes of olfactory-mediated behavioural impairment. By contrast, experiments simulating future ocean acidification suggest that interference of high CO2 with brain neurotransmitter function is the primary cause for olfactory-mediated behavioural impairment in fish. Different physico-chemical characteristics between marine and freshwater systems are probably responsible for these distinct mechanisms of impairment, which, under globally rising CO2 levels, may lead to strikingly different consequences to olfaction. While fluctuations in pH may occur in both freshwater and marine ecosystems, marine habitat will remain alkaline despite future ocean acidification caused by globally rising CO2 levels. In this synthesis, we argue that ecosystem-specific mechanisms affecting olfaction need to be considered for effective management and conservation practices.

1. Introduction

Anthropogenic acidification of lakes, rivers and the oceans can have dramatic and far-reaching impacts on the structure and function of aquatic ecosystems [1–5]. Historically, the problem of acidification has mostly been associated with freshwater ecosystems affected by acid rain precipitation [6–8]. Decades of this phenomenon have reduced the acid neutralizing capacity in many impacted areas, leading to persisting vulnerability of freshwater ecosystems to future changes of water pH [9,10]. However, attention has shifted towards the threat of acidification in marine ecosystems, as increased CO2 uptake from the atmosphere is causing ocean pH to decline with a concomitant increase in dissolved CO2 [5,11]. Although the mechanism of anthropogenic acidification differs between freshwater and marine ecosystems (box 1), the underlying cause is the same—the continued burning of fossil fuels (figure 1). Furthermore, the chemical changes associated with acidification can lead to fundamental changes to biological and ecological processes in both freshwater and marine ecosystems, including impacts on individual performance (e.g. reproductive output or predator avoidance), species interactions and community structure [7,11,19].
For many aquatic organisms, one of the main consequences of non-lethal acidification of aquatic ecosystems may be the disruption of olfaction and chemosensory abilities [20,21]. The detection of chemical cues and signals by olfactory and gustatory receptors plays a central role in the decision-making process [22], especially in structurally complex or turbid environments or under low light conditions [23–25]. For instance, homing [26,27], microhabitat choice [28,29], mate selection [30,31], kin recognition [32], food location [33], dominance interactions [34] and predator avoidance [35,36] are all mediated by the detection of chemical cues, at least to some extent. Any interference with the functioning of normal chemosensory responses could reduce the ability to perceive basic environmental stimuli or public information that is critical for long-term survival. Consequently, impaired olfactory-mediated responses caused by acidification in freshwater and marine ecosystems may have significant impacts on the ecology and life histories of many aquatic organisms. Experiments with freshwater fish have demonstrated a range of behavioural and ecological changes associated with the impairment of olfaction and chemical cues detection under weakly acidified conditions (approx. pH 6.0) [20,37,38]. Recently, a very similar range of behavioural changes has been observed in experiments with marine fish exposed to predicted future changes in ocean pH due to rising atmospheric CO$_2$ [39,40]. However, despite the remarkable similarity in many of the behavioural responses, the underlying mechanisms appear to be entirely different [37,41]. In this review, we compare and contrast the effects of acidification on olfactory-mediated behaviour in freshwater and marine organisms and present evidence for significant dissimilarities between the underlying mechanisms of action. Numerous studies demonstrating these effects have used fish as a model organism, whereas studies using invertebrates are by comparison much rarer. Reflecting this asymmetry, we mostly used fish examples to explore this question and included invertebrates examples when available. We then consider how projected increases in atmospheric CO$_2$ may affect marine and freshwater organisms. Identifying the consequences of acidification on olfactory-mediated behaviour, along with understanding of the mechanisms at play become critical for applying effective management and conservation practices in freshwater and marine ecosystems.

2. Ecological effects of acidification on olfaction

(a) Freshwater ecosystems

Experiments in freshwater have demonstrated that the ability of fishes to detect and respond to chemical cues of injured conspecifics (termed ‘alarm cues’ [24,25]) may be disrupted under weakly acidified conditions. Alarm cues are particularly useful for studying chemosensory abilities in fishes as they trigger innate, readily measurable overt responses [24,42]. Exposure to alarm cues can elicit adaptive predator avoidance behaviour, such as reduced activity levels and increased hiding or tighter group cohesion [43]. These behavioural responses to alarm cues have been observed in a range of freshwater fishes, including fathead minnows (Pimephales promelas), finescale dace (Phoxinus neogaeus), pumpkinseed (Lepomis gibbosus) and rainbow trout (Oncorhynchus mykiss) [20,37,44]. However, predator avoidance behaviour was diminished or absent when these alarm cues were presented in experimental treatments acidified using a minute amount of sulfuric acid (often a major contributor to freshwater acidification) [20,38,45]. Furthermore, behavioural responses to basic chemical stimuli from food (amino acids) were significantly reduced under a similar range of pHs (e.g. 5.0–6.0) in fathead minnows and Atlantic salmon (Salmo salar) [38,46]. Under field conditions, experiments revealed a similar absence of response to chemosensory cues in brook trout (Salvelinus fontinalis) and Atlantic salmon exposed to conspecific alarm cues in acidic streams (pH range; 5.8–6.3), whereas avoidance responses were retained in neutral pH streams (pH range; 6.8–7.4) [20,45,47,48]. Likewise, episodic acidifying events may cause short-term loss of chemosensory abilities in freshwater fish. Field tests demonstrated that following acid rain precipitations, the response of Atlantic salmon to alarm cues did not differ from their response to a control stimulus of stream water (at approx. pH 6.2) [45]. Following subsequent flushing of the acid pulses, the response of the salmon returned to pre-acidification levels.
(approx. pH 6.9) and they exhibited strong predator avoidance behaviour in the presence of the alarm cues. Together, these experiments and observations demonstrate that even relatively small changes in pH (approx. 0.5 unit) can dramatically affect both the feeding and antipredator responses of freshwater fishes. Such demonstrated loss of adaptive alarm behaviour under weakly acidic conditions is probably due to an inability to detect and thus respond to alarm cues. Indeed, following the pairing of aversive alarm cues stimulus with a novel odour, wild Atlantic salmon tested in neutral streams subsequently responded to the novel odour as a dangerous stimulus [49]. However, following the same procedure, similar learned responses did not occur for salmon conditioned and tested in acidic streams, suggesting a pH-mediated inability to perceive the information of risk that is normally associated with the alarm cues [50]. Under acidified conditions, the lack of antipredator response towards the alarm cues probably prevents the learned association of risk with the novel predator odour, resulting in failed learning. Thus, the retention of and the ability to generalize acquired predatory recognition may be significantly impaired under weakly acidic conditions [51,52].

Failure to appropriately respond to chemical cues could significantly increase mortality rates of prey and potentially alter population dynamics. The ecological consequence of pH-mediated chemosensory impairment to chemical alarm cues was demonstrated in staged encounters between rainbow trout prey and a predator, the largemouth bass (Micropterus salmoides). Bass captured trout faster and in greater proportion when trout alarm cues introduced in test tanks were acidified (pH 6.0) compared with treatments were alarm cues were introduced using neutral pH water [48]. Thus, prey ‘naïveté’ arising from acid-mediated chemosensory impairment led to greater predation cost. In addition to alarm behaviour, weak acidification may affect other behavioural activities in freshwater fishes. Suppression of spawning [53], nest digging [54] and migration behaviour [55] were demonstrated in landlocked sockeye salmon (Oncorhynchus nerka) exposed to weak levels of acidification (i.e. pH 6.1–6.3). Thus, non-lethal anthropogenic acidification may affect a wide range of behaviour in freshwater fishes, with significant effects on their life histories and role in the ecosystem. Although providing important insights to the potential ecological consequences of acidity-mediated maladaptive behaviour, the studies mentioned above were conducted under controlled laboratory conditions. Future studies would further this knowledge, while providing ecologically relevant data, by conducting investigations under field conditions.

Akin to fish olfaction abilities, experimental evidence demonstrated that freshwater invertebrates may, likewise, be affected by acidification. In crayfishes, Orconectes virilis and Procambarus acutus, weakly acidified conditions (pH 5.8) had no effect on feeding behaviour to an amino acids mixture but more severe acidification levels (pH 4.5 and 3.5) led to significant reductions of this response [56]. Interestingly, in this experiment the amount of food consumed was not affected by acidification, suggesting that compared with fishes, these crustaceans may have higher tolerance towards acidification. Similar olfaction impairment was also demonstrated in the crayfish Cambarus baroni, which showed reduced ability to detect a food source at pH 4.5 [57].

(b) Marine ecosystems

Atmospheric CO₂ has increased from approximately 280 ppm at the start of the industrial revolution to over 390 ppm today, and there has been a corresponding 0.1 pH unit decline in ocean pH [16]. Depending on emission scenarios, CO₂ levels in the atmosphere could exceed 900 ppm by the end of the century [58]. This would cause the pH of the ocean to drop another 0.3–0.4 units. Under such scenarios of future oceanic acidification, the ability of larval orange clownfish (Amphiprion percula) to discriminate between olfactory cues involved in the selection of suitable settlement sites was tested [21]. Larval clownfish reared in control seawater (today’s pH of 8.15) had the ability to discriminate between chemical cues of suitable versus unsuitable settlement sites and between kin and non-kin. However, when larvae were reared from hatching under conditions simulating near-future CO₂-induced ocean acidification (pH 7.8 and 1050 ppm CO₂), this discriminatory ability was lost and larvae became attracted to olfactory stimuli that they normally avoided. Similarly, five-lined cardinalfish (Cheilodipterus quinquelineatus) exposed to future conditions...
demonstrated that clownfish and wild-caught damselfish cues of predators and non-predators [60]. Further experiments demonstrated that clownfish and wild-caught damselfish (Pomacentrus wardi) reared under high CO2 treatments (700 and 850 ppm CO2) for only 2–4 days also displayed impaired olfactory-mediated behaviour, whereby CO2-treated fish initially avoided predator odour, as did control fish, but subsequently became attracted to this odour [61].

Similar to the loss of alarm response in freshwater fishes, laboratory tests revealed that juvenile damselfish exposed to CO2-acidified conditions for 4 days exhibited a decreased response to conspecific chemical alarm cues [62]. The response of predators to prey alarm cues was also affected, with a common predator of juvenile damselfishes, the brown dottyback (Pseudochromis fuscus), spending approximately 20% less time in a water stream containing prey odour following exposure to near-future CO2-acidification conditions [62,63]. Reduced attraction to prey odour by the predator did not, however, offset an increased risk of predation in prey fish exposed to elevated CO2. Mortality rates of small damselfishes were almost twice that of controls when a high CO2-exposed dottyback interacted with high CO2-exposed damselfish in a mesocosm experiment [62].

Field tests conducted in natural habitat revealed significant ecological outcomes of behavioural changes caused by predicted ocean acidification. Juvenile damselfish exposed to CO2-acidified conditions and then placed on patches of coral habitats were more active and ventured further from shelter than juveniles exposed to current-day CO2 levels [61,62]. This riskier behaviour was associated with increased mortality from predation when compared with control fish [61,62]. Reduced olfaction abilities and other cognitive impairment that occurs at elevated CO2 levels [41,64,65] also appear to affect navigation and homing of reef fish under natural conditions. For instance, cardinalfish uses olfactory cues and visual landmarks to aid in navigation to daytime resting sites after nocturnal foraging, but cardinalfish reared under elevated CO2 treatments displayed a 22–31% reduction in homing success compared with control fish when released at 200 m from home sites [66]. Despite showing home-site fidelity, high CO2-treated fish were more active and ventured further from the reef compared with control fish [66], which would be likely to increase their risk of predation. Given that the persistence of most coastal species depends on the ability of larvae to find suitable settlement sites and avoid predators at the end of their pelagic phase, the effects of ocean acidification on habitat selection and predator avoidance behaviour may have significant consequences for the replenishment of fish populations. Furthermore, variation in sensitivity to acidification among prey species [67] and shifts in prey preference by predators [62] could lead to far-reaching effects on reef fish community structure.

In addition to predator–prey interactions and homing behaviour, changes in seawater pH may also have consequences on mate choice and reproductive behaviour. For instance, females may choose between males using major histocompatibility complex (MHC) alleles, which may be perceivable through scent [68,69]. In a laboratory choice experiment, gravid female stickleback (Gasterosteus aculeatus) were more attracted to male olfactory cues when pH was raised from 8.0 to 9.5 using NaOH [70]. In pipefish (Syngnathus typhle), a similar pH increase through Na2CO3 addition reduced the number of pregnant males [71]. Reducing seawater pH to 7.5 with CO2 had no effect on mating propensity in the pipefish [71], however the duration of exposure to acidified conditions (less than 5 h total) was probably insufficient for any behavioural effects of elevated CO2 to be induced [61]. While these examples demonstrated effects of seawater alkalinization through eutrophication, rather than its acidification by rising CO2 levels, they underscore that changes in seawater pH may alter important processes in sexual selection. At present, a gap in knowledge exists limiting our ability to predict if near-future ocean acidification scenarios will have similar effects on mate choice.

In marine invertebrates, acidification has been shown to detrimentally affect behavioural choices at very low pH. In hermit crabs (Pagurus bernhardus), finding and selecting the gastropod shells they inhabit is conducted via tactile, visual and chemical assessment. Choosing an optimal shell is vital as it provides protection against environmental extremes and predators. Under highly acidified conditions (pH 6.8 and 12 000 ppm CO2), crabs were less likely to change from a sub-optimal to an optimal shell than those in untreated seawater, while the time required to change shells significantly increased [72]. Additionally, at this reduced pH level, hermit crabs were less successful in locating an odour source and had lower locomotory activity compared with hermit crabs in untreated seawater [73]. Thus, reductions in seawater pH may have disruptive consequence on resource assessment and gathering along with the decision-making processes of hermit crabs. Whether these impaired response patterns occur at more representative future levels of ocean acidification (CO2 levels <1000 ppm) and are generalizable in marine invertebrates is unknown.

3. Mechanisms of behavioural impairment

Although olfaction impairment in freshwater and marine organisms exposed to acidified conditions may have very similar consequences on behaviour (table 1), translating into equivalently significant ecological costs (e.g. increased predation, reduced recruitment), given the different modes of acidification between freshwater and marine habitat, the mechanisms affecting olfactory/chemosensory response appear to be entirely distinct.

(a) Freshwater ecosystems

In freshwater, acidification may affect fish olfaction by two non-mutually exclusive mechanisms. First, reduced chemosensory abilities observed in acidified conditions can stem from molecular change to chemical cues, essentially rendering them as ‘non-functional’ [37]. For example, the alarm cues of Ostariophyian fishes probably consist of a suite of active compounds such as purine-N-oxides [30,68] and glycosaminoglycan chondroitins [79]. Analytical chemical work has suggested that under acidic conditions, one of these active components, hypoxanthine-3-N-oxide is converted to 6,8-dioxypurine with a loss of the 3-N-oxide functional group [80,81] (figure 2). This suggests that acute exposures to acidic conditions might result in the non-reversible loss of the N–O functional group, reducing the effectiveness of the alarm cue to elicit an adaptive alarm response [82]. It is

of CO2 demonstrated significantly reduced abilities to discriminate between odours of their home site versus a foreign site [59]. In another study, aquarium-reared larval clownfish under acidified conditions became attracted to the odour of predators and were unable to distinguish between the chemical cues of predators and non-predators [60]. Further experiments demonstrated that clownfish and wild-caught damselfish (Pomacentrus wardi) reared under high CO2 treatments (700 and 850 ppm CO2) for only 2–4 days also displayed impaired olfactory-mediated behaviour, whereby CO2-treated fish initially avoided predator odour, as did control fish, but subsequently became attracted to this odour [61].
Table 1. Effects of acidification/alkalinization on olfactory/chemosensory abilities and its consequences in fish and invertebrate species. PC, post-conditioning; RTE, reciprocal transfer experiment.

<table>
<thead>
<tr>
<th>species</th>
<th>type of cue</th>
<th>behavioural response</th>
<th>treatment/environmental change and range</th>
<th>consequence</th>
<th>references</th>
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<td>freshwater</td>
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<td><em>Pimephales promelas</em></td>
<td>food stimulus</td>
<td>food searching</td>
<td>acidification (H₂SO₄)</td>
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<td>[38]</td>
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<td></td>
<td></td>
<td></td>
<td>pH 6.5</td>
<td>neutral</td>
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<td></td>
<td>pH 6.0</td>
<td>negative</td>
<td></td>
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<tr>
<td><em>Poecilia sphenops</em></td>
<td>food stimulus</td>
<td>food searching</td>
<td>acidification (H₂SO₄)</td>
<td></td>
<td>[74]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>pH 6.0</td>
<td>neutral</td>
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<td></td>
<td>pH 5.0</td>
<td>negative</td>
<td></td>
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<tr>
<td><em>Salmo salar</em></td>
<td>L-serine</td>
<td>odour discrimination</td>
<td>acidification (HNO₃) and H₂SO₄</td>
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<td>[46]</td>
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<td></td>
<td>alanine</td>
<td></td>
<td>pH 5.1</td>
<td>negative</td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td>pH 5.1</td>
<td>positive</td>
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<td><em>Onchorynchus mykiss</em></td>
<td>L-serine</td>
<td>electro-physiological response</td>
<td>acidification (H₂SO₄)</td>
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<td>[75]</td>
</tr>
<tr>
<td></td>
<td>amino acids</td>
<td>food searching</td>
<td>acidification (H₂SO₄)</td>
<td></td>
<td>[56]</td>
</tr>
<tr>
<td></td>
<td>mixture</td>
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<td>pH 6.8</td>
<td>neutral</td>
<td></td>
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<td></td>
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<td>pH 5.8</td>
<td>neutral</td>
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<td>pH 4.5</td>
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<td>pH 3.5</td>
<td>negative</td>
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<tr>
<td><em>Cambarus bartoni</em></td>
<td>food stimulus</td>
<td>food searching</td>
<td>acidification (H₂SO₄)</td>
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<td>[57]</td>
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<td></td>
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<td>pH 7.5</td>
<td>neutral</td>
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<td>pH 4.5</td>
<td>negative</td>
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<td></td>
<td></td>
<td>pH 7.5</td>
<td>negative</td>
<td></td>
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<td><em>S. salar</em></td>
<td>testosterone, ovulated female urine</td>
<td>electro-physiological response</td>
<td>acidification (H₂SO₄)</td>
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<td>[76]</td>
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<td></td>
<td></td>
<td>pH 6.5 – 3.5</td>
<td>increasingly negative</td>
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<td></td>
<td>pH 8.5 – 9.5</td>
<td>increasingly negative</td>
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<td><em>Pimephales promelas</em>, <em>Phoxinus neogaeus</em></td>
<td>conspecific skin extract, hypoxanthine-3-N-oxide</td>
<td>alarm response</td>
<td>acidification (H₂SO₄)</td>
<td></td>
<td>[37]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>pH 6.0</td>
<td>negative</td>
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<tr>
<td><em>Lepomis gibbosus</em></td>
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<td>alarm response</td>
<td>acidification (H₂SO₄)</td>
<td></td>
<td>[44]</td>
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<td></td>
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<td>pH 6.0</td>
<td>negative</td>
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<td></td>
<td></td>
<td>pH 6.0</td>
<td>negative</td>
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<tr>
<th>species</th>
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<th>behavioural response</th>
<th>treatment/environmental change and range</th>
<th>consequence</th>
<th>references</th>
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<tr>
<td><em>O. mykiss</em></td>
<td>conspecific skin extract</td>
<td>alarm response</td>
<td>acidification (H₂SO₄), pH 6.0</td>
<td>negative</td>
<td>[20]</td>
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<td><em>Salvelinus fontinalis</em></td>
<td>conspecific skin extract</td>
<td>—</td>
<td>stream acidification, pH ≈ 6.1</td>
<td>negative</td>
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<td><em>S. salar</em></td>
<td>conspecific skin extract</td>
<td>alarm response</td>
<td>acidic rain, pH 6.2</td>
<td>negative</td>
<td>[45]</td>
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<td><em>O. mykiss</em></td>
<td>—</td>
<td>survival to predator</td>
<td>acidification (H₂SO₄), pH 6.0</td>
<td>negative</td>
<td></td>
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<tr>
<td><em>S. salar</em></td>
<td>conspecific skin extract</td>
<td>alarm response</td>
<td>stream acidification, pH 5.8 – 6.1</td>
<td>negative</td>
<td>[47]</td>
</tr>
<tr>
<td><em>S. salar</em></td>
<td>conspecific skin extract, lemon odour</td>
<td>acquired predator recognition conditioning</td>
<td>pH ≈ 6.1</td>
<td>negative</td>
<td>[50]</td>
</tr>
<tr>
<td><em>O. mykiss</em></td>
<td>conspecific skin extract, predator odour</td>
<td>acquired predator recognition conditioning</td>
<td>pH 6.0</td>
<td>negative</td>
<td>[51]</td>
</tr>
<tr>
<td><em>S. salar</em></td>
<td>conspecific skin extract</td>
<td>alarm response</td>
<td>stream acidification, pH ≈ 6.1</td>
<td>negative</td>
<td>[77]</td>
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<td><em>Gasterosteus aculeatus</em></td>
<td>male odour</td>
<td>mate choice</td>
<td>alkalization (NaOH), pH 9.5</td>
<td>positive</td>
<td>[70]</td>
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<td><em>Pomacentrus moluccensis, P. amboinensis, P. chrysurus</em></td>
<td>habitat odour</td>
<td>habitat choice</td>
<td>elevated carbon dioxide, 700, 850 ppm CO₂</td>
<td>negative</td>
<td>[59]</td>
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<tr>
<td><em>Cheilodipterus quinquelineatus</em></td>
<td>habitat odour</td>
<td>habitat choice</td>
<td>elevated carbon dioxide, 550 – 950 ppm CO₂</td>
<td>negative</td>
<td>[66]</td>
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<tr>
<td><em>Amphiprion percula</em></td>
<td>habitat odour, conspecific odour</td>
<td>habitat choice/homing</td>
<td>acidification, elevated carbon dioxide, pH 7.8, 1050 ppm CO₂</td>
<td>negative</td>
<td>[21]</td>
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<tr>
<td><em>Pagurus bernhardus</em>¹</td>
<td>gastropod shell cues</td>
<td>resources assessment</td>
<td>acidification, elevated carbon dioxide, pH 6.8, 12 000 ppm CO₂</td>
<td>negative</td>
<td>[72]</td>
</tr>
<tr>
<td><em>Pagurus bernhardus</em>²</td>
<td>food odour</td>
<td>food searching</td>
<td>acidification, elevated carbon dioxide, pH 6.8, 12 000 µatm CO₂</td>
<td>negative</td>
<td>[73]</td>
</tr>
<tr>
<td><em>A. percula</em></td>
<td>predator odour</td>
<td>avoidance</td>
<td>acidification, elevated carbon dioxide, pH 7.8, 1000 ppm CO₂</td>
<td>negative</td>
<td>[60]</td>
</tr>
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(Continued.)
unknown, but likely that changes in pH also affect chondroitin functionality as well. In keeping with the hypothesis of an irreversible molecular change to the chemical cue, short-term (48 h) changes in water pH, from neutral to weakly acidic and back to neutral, were well matched with the ability of fish to detect and respond to the alarm cues [37]. This experimental design suggested that no permanent olfactory damage or significant stress could account for the loss of response observed at the acidity level tested (pH 6.0). Similarly, a reverse transplant experiment, in which Atlantic salmon from either neutral or acidic streams were alternatively tested in their natal stream or in a stream of a different pH, demonstrated that the rearing pH was not directly affecting salmon chemosensory detection abilities. After a 24 h period of acclimation in stream enclosures, the response to chemical alarm cues was detectable in all salmon (reared in neutral or acidic streams) when tested under neutral but not under acidic streams [77]. Thus, under acidic condition, the alarm cues

**Table 1.** (Continued.)

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<td><em>Plectropomus leopardus</em></td>
<td>predator odour</td>
<td>antipredator</td>
<td>elevated carbon dioxide</td>
<td>negative</td>
<td>[78]</td>
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<td></td>
<td></td>
<td></td>
<td>700 – 850 μatm CO₂</td>
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<tr>
<td><em>A. percula</em></td>
<td>predator odour</td>
<td>predator discrimination</td>
<td>elevated carbon dioxide, GABA-A receptor antagonist</td>
<td>neutral</td>
<td>[41]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>900 μatm CO₂</td>
<td></td>
<td></td>
</tr>
<tr>
<td><em>A. percula</em></td>
<td>predator odour</td>
<td>antipredator</td>
<td>elevated carbon dioxide</td>
<td>negative</td>
<td>[61]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>550 ppm CO₂</td>
<td></td>
<td></td>
</tr>
<tr>
<td><em>Pomacentrus wardi</em></td>
<td>live predators</td>
<td>antipredator</td>
<td>elevated carbon dioxide</td>
<td>negative</td>
<td>[77]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>700 ppm CO₂</td>
<td></td>
<td></td>
</tr>
<tr>
<td><em>P. moluccensis,</em> <em>P. amboinensis,</em> <em>P. nagasakiensis,</em> <em>P. chrysurus</em></td>
<td>live predator</td>
<td>predator avoidance</td>
<td>elevated carbon dioxide</td>
<td>negative</td>
<td>[62]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>700 μatm CO₂</td>
<td></td>
<td></td>
</tr>
<tr>
<td><em>Pseudochromis fuscus</em></td>
<td>live prey</td>
<td>prey selection</td>
<td>elevated carbon dioxide</td>
<td>reversed preferred size selection</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>700 μatm CO₂</td>
<td></td>
<td></td>
</tr>
<tr>
<td><em>P. moluccensis,</em> <em>P. chrysurus,</em> <em>P. amboinensis</em> <em>P. nagasakiensis</em></td>
<td>conspecific skin extract</td>
<td>antipredator</td>
<td>elevated carbon dioxide</td>
<td>negative</td>
<td>[67]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>700 – 850 ppm CO₂</td>
<td></td>
<td></td>
</tr>
<tr>
<td><em>P. chrysurus</em></td>
<td>live predators</td>
<td>survival</td>
<td>elevated carbon dioxide</td>
<td>negative</td>
<td>[65]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>700 – 850 ppm CO₂</td>
<td></td>
<td></td>
</tr>
<tr>
<td><em>Pseudochromis fuscus</em></td>
<td>prey skin extract</td>
<td>prey odour discrimination</td>
<td>acidification, elevated carbon dioxide</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>pH 8.0, 630 μatm CO₂</td>
<td>negative</td>
<td></td>
</tr>
<tr>
<td><em>Pomacentrus amboinensis</em></td>
<td>conspecific skin extract, predator odour</td>
<td>acquired predator recognition</td>
<td>acidification, elevated carbon dioxide</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>pH 7.9, 850 ppm CO₂</td>
<td>negative</td>
<td></td>
</tr>
</tbody>
</table>

*aInvertebrate.

*bConducted sequentially.

*cExperiments conducted under field conditions.*
Figure 2. Potential mechanisms leading to olfactory-mediated behavioural impairment in freshwater (a) and marine fishes (b). (a) In the Ostariophysi alarm cue molecule (hypoxanthine-3-N-oxide), at neutral pH the acid–base equilibrium heavily favours the deprotonated (N–O<N) form (i). However, as the pH decreases, the acid–base equilibrium shifts in favour of the hydroxy form (ii), decreasing the relative concentration of the deprotonated active form of the chemical signal. Modified from Brown et al. [61]. (b) In marine fish, physiological interferences arising from the hyperpolarization of the neurotransmitter membrane of the GABA-A receptor occur when exposed to elevated CO2-acidified conditions. Adapted from Nilsson et al. [39]. (Online version in colour.)

appear to undergo molecular changes and become either completely degraded (i.e. non-functional) and unrecognizable, or the concentration of its active component is reduced below a threshold necessary to trigger an adaptive alarm response [44].

A second mechanism by which olfaction and chemosensory abilities may be affected stems from physiological disruptions of the fishes’ olfactory organs, whereby reduced sensitivity or affinitivity to fish olfactory receptors may occur [74,76,83]. In rainbow trout, fathead minnow and Atlantic salmon, reduced abilities to respond to amino acids or ovulated female urine were demonstrated at approx. pH 6.0 [38,46,76]. Similar to the pH-dependent response observed for chemical alarm cues, the feeding response to amino acids was well matched with short-term changes in water pH. Indeed, Atlantic salmon were attracted to glycine under neutral pH (7.6) but became indifferent under lower tank pH (5.1), while following a return to neutrality, salmon olfactory attraction towards glycine was re-activated [46]. Importantly, these short-term effects may be magnified in heavily acidified conditions (i.e. pH < 6.0) under which the release of monomeric ions (Al<sup>3+</sup>, Cu<sup>2+</sup>) may further interfere with olfactory epithelia, leading to lasting chemosensory impairment [75,76].

Intriguingly, in freshwater systems, the ability of fishes to detect chemical cues may not be steadily affected by acidification. For instance, the time required of gold mollies (Poecilia sphenops) to locate food sources was not significantly different between pH 6.0 and pH 7.9 [74]. Likewise, the pH of a novel odour was not a critical factor for its subsequent recognition as a danger stimulus by juvenile rainbow trout, as long as it was paired with chemical alarm cues that were left unacidified [84]. Thus, in freshwater, acidification does not appear to systematically affect fish chemosensory abilities and olfactory receptor sensitivity. However, as described earlier, the chemical nature of the alarm cues appears to be modified, thereby reducing their effectiveness to trigger a response [37]. For this later mechanism of impairment, a threshold for chemosensory detection has been shown to occur at a pH of approximately 6.3, whereby rainbow trout failed to respond to chemical alarm cues [85]. Likewise, electro-physiological recordings of Atlantic salmon olfactory epithelia were significantly reduced at a pH of 5.5 [76]. Several variables could affect such a potential threshold of chemosensory impairment, including the species under investigation along with the chemical compounds tested. However, experimental results performed close to these thresholds indicate that chemosensory impairment may be readily reversed following a return of ambient water to neutral pH [37,46,76,85], thereby suggesting that weak acidification does not have lasting physiological consequences to fish olfaction.

(b) Marine ecosystems

In contrast to the findings in freshwater fishes, CO2-induced acidification affects the behavioural response of marine fish to chemical cues, but does not appear to affect the cue itself. Orange clownfish larvae reared in control conditions (pH 8.15) but immediately tested in acidified conditions (pH 7.6) exhibited the same odour choices as larvae reared and immediately tested in control water. Larvae reared at pH 7.6 but tested in control water did not respond to any olfactory stimuli, just as larvae reared and tested at pH 7.6 water did not respond to odours [21]. This demonstrates that rearing the fish in acidified conditions causes the behavioural changes, and that the pH of seawater does not seem to affect the cue, at least for a change in pH of 0.5 unit. Likewise, using a classical conditioning design, pre-settlement damsel-fish (Pomacentrus amboinensis) reared in control water were
able to associate a novel predator odour as a stimulus of danger when the novel odour was paired with innately aver-
sive alarm cues. However, this ability was compromised in
damselﬁsh larvae reared in acidiﬁed water for 4 days, despite
holding the recognition phases of the novel predator odour in
control water [86]. Overall, these results show that exposures
to CO₂-acidiﬁed water affect the olfactory system and that
the observed changes are not caused by an immediate inter-
ference to the fishes’ olfactory capabilities or chemical
modiﬁcation of the odour cues.

The mechanism accounting for a loss of olfaction and
chemosensory abilities in marine ﬁshes exposed to acidiﬁed
conditions appears to stem from a disruption of the normal
Cl⁻ and/or HCO₃⁻ gradients over neuronal membranes,
causing some GABA-A receptors to become excitatory (depolar-
izing) rather than inhibitory (hyperpolarizing) [41]. The
GABA-A receptor, which is the major inhibitory neurotrans-
mitt receptor in vertebrate brains, normally hyperpolarizes
neuronal membranes by opening a channel that leads to an
inﬂux of Cl⁻ and HCO₃⁻. When exposed to high CO₂,
marine ﬁshes regulate their acid–base balance by accumulat-
ing HCO₃⁻, with compensatory reductions in Cl⁻ [87]. In the
brain, this may lead to disturbances of the normal Cl⁻ and/or HCO₃⁻
gradients in some neurons, resulting in gradients that favour
inﬂux rather than out ﬂux of these anions. Changes in HCO₃⁻
and Cl⁻ levels during high CO₂ exposures thereby affect
behaviour and cause dramatic shifts in sensory choices [41].
Consequently, it is not the change in seawater pH that impairs
olfaction and chemosensory abilities in marine ﬁshes but
rather the long-term exposure to elevated levels of environ-
mental CO₂. This is a critical distinction between the effects
of acidification in freshwater systems that occurs as a result of
mineral acids, and acidification in marine systems, which is
occurring owing to increased uptake of atmospheric CO₂.

Aside from olfaction, neurotransmitter disruption caused
by elevated CO₂ levels has far-ranging effects on ﬁshes’ be-
behaviour. For instance, elevated CO₂ levels led to increased
activity levels in ﬁsh [61,78] and interfered with auditory
preferences, whereby no avoidance behaviour occurred
during playbacks of predator-rich daytime reef recordings
[88]. Furthermore, elevated CO₂ repressed the degree of be-
havioural lateralization, with individual propensity to turn
left or right becoming random under elevated CO₂ [64].
Interestingly, treatments using a speciﬁc GABA-A receptor
antagonist (gabazine) administered 30 min before behavio-
ural assays restored behavioural responses in clownﬁsh,
(A. percula) that had been reared for 11 days in acidiﬁed con-
ditions. When tested prior to administration of the receptor
antagonist, the ﬁsh exhibited abnormal responses to chemical
cues for a predatory ﬁsh. By contrast, they displayed similar
olfaction abilities as ﬁsh reared in control conditions follow-
ing the administration of the receptor antagonist, indicating
that altered GABA-A receptor activity mediates the effects
of high CO₂ on neural function in marine ﬁshes, including
reversal of olfactory responses [41]. Although neurophysiolo-
cal stress triggered by high CO₂ may lead to olfactory-mediated
maladaptive behaviour, it is unknown to what extent the
concomitant changes in pH predicted under future ocean acid-
ification scenarios may directly affect the chemosensory cues.
Behavioural tests conducted under a range of pH while keeping
CO₂ constant would resolve this question.

As it pertains to organisms living in brackish conditions
(e.g. estuarine ecosystems), little is known about the potential
effects of acidiﬁcation on olfactory-mediated behaviour. Euro-
pean eels (Anguilla Anguilla) demonstrated a surprisingly
high level of physiological tolerance towards hypercapnia
[89,90]. Although these experiments were conducted in fresh-
water, such tolerance to hypercapnia is greater than what
can be expected from most teleost ﬁsh. Studies conducted on
Atlantic salmon demonstrated that osmotic stress might be
ampliﬁed when exposed to acidification [91–93]. As such, it
is not well known how the chemosensory ability of organisms
found in brackish waters will be affected by acidification.
Likewise, for aquatic invertebrates little is known regarding
the mechanisms affecting chemosensory abilities under
freshwater or marine acidification.

4. Why the difference in response mechanisms?

A critical question arising from the research conducted to date
in freshwater and marine ecosystems is why different mechan-
isms should be responsible for otherwise similar effects of
acidification on olfactory responses in these two ecosystems.
In what way are freshwater and marine ecosystems fundamen-
tally different in their respective acidification processes that
affect olfactory functions in aquatic organisms? Answering
these questions is important for predicting the effects of differ-
ent forms of anthropogenic acidiﬁcation in aquatic systems.

A useful way to contextualize the cause of an apparently
similar impairment to chemosensory functions between
freshwater and marine ecosystems involves comparing their
inherent characteristics of acidification. Freshwater ecosys-
tems often have a pH that is near neutrality but can also be
acidic or alkaline. By contrast, seawater always remains alka-
line. Thus, it might not be the change in pH level but rather
the absolute pH value that determines the non-reversible
changes in chemical alarm cues and impairs olfactory neu-
rons in freshwater ﬁshes, but not in marine ﬁshes. In
freshwater systems, behavioural impairment has been
shown to start occurring in mildly acidic conditions (6.3–
6.5), becoming very evident as pH decreases [38,76,87]. By
contrast, predicted ocean acidification will bring seawater
pH to a more acidic value, but it will still remain alkaline
(i.e. above pH 7.0). In fact, ocean acidification experiments
never get close to the pH levels under which olfaction is
impaired in freshwater. Thus, compared with marine ﬁshes,
freshwater ﬁshes may tend to live in more acidic conditions
and therefore closer to the threshold under which the struc-
ture of the chemical alarm cues is changed [37,85] or the
sensitivity of olfactory neurons is affected [38,46,76]. The
chemical bonds of alarm cue molecules, and probably other
odour molecules, are probably sensitive to the absolute pH
they experience, not just a change in pH per se [51,52]. There-
fore, the reason why studies on acidification in freshwater
have found that changes to chemical stimuli are responsible
for altered behaviour, whereas this does not appear to be
the case in marine studies, is probably that they are working
in different parts of the pH scale (i.e. weakly acidic freshwater
versus weakly alkaline ocean water).

In addition to absolute pH levels, the absolute pCO₂ level
experienced is also critical for understanding the potential
causal mechanism of olfactory-mediated maladaptive behav-
ior detected in ﬁsh. In ocean acidification studies, both the
pH and pCO₂ are manipulated, whereas in freshwater acid-
ification studies only pH is manipulated. This reﬂects the
different mechanism of acidification in these two ecosystems, and there are important considerations that emerge from these differences in experimental approach. First, although the pH of seawater is usually much higher than that of freshwater when both are in equilibrium with the atmosphere (and thus have approximately the same $p$CO$_2$), freshwater studies have not manipulated pCO$_2$ levels. Consequently, it is impossible to conclude that freshwater fishes are more tolerant to acidification than marine fishes simply because their behaviour is not affected at the pH levels at which marine fishes are highly affected. Secondly, if pCO$_2$ remains relatively unchanged in freshwater that is acidified by acids, because any CO$_2$ generated is rapidly equilibrated with the atmosphere, then a similar mechanism of behavioural change cannot be expected to occur in freshwater fishes compared with marine fishes that are exposed to increased pCO$_2$. At identical pH levels, there is evidence that CO$_2$ has greater negative impacts on aquatic organisms when compared with mineral acids [94,95]. However, further research is needed to carefully elucidate the various effects of pH and pCO$_2$ in ocean acidification research. Considering freshwater fishes, it is unknown whether their sensitivity to increasing pCO$_2$ is the same as in marine fishes. It is possible that freshwater fishes might be less sensitive to future changes in pCO$_2$ than marine fishes, but to our knowledge this hypothesis has not been tested.

5. Environmental variability and adaptations

In order to understand the potential consequences of anthropogenic acidification on olfactory functions of freshwater and marine organisms, it is necessary to consider the spatial and temporal variation of pH and pCO$_2$ in their native habitats. Species living in environments that naturally experience significant variation in pH and/or pCO$_2$ may be adapted to this variation, and thus may be more tolerant of anthropogenic acidification compared with species living in more stable pH and pCO$_2$ environments [96,97]. In freshwater ecosystems, the magnitude of pH changes may be substantial. For example, short-term rainfall events (i.e. approx. 30 mm) may be sufficient to reduce ambient acidity by 0.2–0.6 pH units [45,98] whereas major rain precipitation events may have more drastic effects on ambient acidity levels [99]. Additionally, in fresh and brackish water with poor buffering capacity, daily fluctuations of nearly 1 pH unit may occur as a function of changing dissolved CO$_2$ concentrations driven by algal metabolism and growth [100,101]. Likewise, in some marine habitats, pH gradients can be quite steep. For example, pH typically fluctuates on a diel cycle in shallow coral reef habitats, changing by more than 0.5 units in some locations [102,103]. The cause of this variation in pH is a change in the balance between the respiratory CO$_2$ production and photosynthetic CO$_2$ consumption of reef organisms, including corals and their symbiotic algae. On shallow reef flats that have restricted water exchange with the open ocean, pCO$_2$ may vary by over 1000 $\mu$atm over 24 h, driving the variation in pH seen in these habitats [104,105]. Variations in pH and pCO$_2$ are generally much less in reef habitats with greater water exchange, but may still shift by more than 0.2 units within a few hours [106], whereas areas of upwelling and coastal habitats can see sharp pH declines that last for days to weeks (approx. 0.4 pH units) [102,107]. Thus, significant shifts in pH may occur in many freshwater and some marine habitats, and this could influence the tolerance to acidification of species living within these particular habitats.

There is evidence for adaptation to acidified habitats in freshwater ecosystems. Natural factors (e.g. rain or snowmelt, high decomposition rates, sulfur oxides/sulfuric acids released from volcanic activity and forest fires) may create extended or even permanent acidification of many freshwater habitats [3,12,108,109]. Associated with these conditions, several freshwater fish species have evolved physiological tolerance towards extreme acidification levels [108,110]. Whether fish in these habitats also experience impaired olfactory-mediated behavioural responses or have evolved tolerance is yet to be tested. Interestingly, a shift in sensitivity of other sensory modalities was shown to occur in juvenile Atlantic salmon inhabiting weakly acidic streams, displaying greater reliance on vision to mediate local predation risks [48]. This suggests that differences in antipredator responses may occur and be linked to the perceived level of information available from different sensory modalities (e.g. from losing chemical information under acidic conditions). However, it might not simply be the range over which pH varies that is important for tolerance to acidification, but also the duration of pH and pCO$_2$ shifts might be critically important. For example, considerable fluctuations in pH and pCO$_2$ may take place in shallow coral reef habitat, but they occur on a regular diel cycle. Low pH and high pCO$_2$ occur at night for a few hours, and the opposite takes place during the day [103–105]. These short-term environmental fluctuations appear to be of insufficient duration to have led to the evolution of tolerance to low pH or high CO$_2$ for extended periods (days) [41,111]. Indeed, maladaptive olfactory-mediated behaviour only starts to occur after at least 24 h exposure to high CO$_2$ [61] in marine fishes. Consequently, a few hours of high CO$_2$ exposure overnight [104,112] is probably of insufficient duration to lead to any discernable effects. A 2–4 day exposure to CO$_2$ conditions similar to that briefly experienced overnight is enough to cause impaired behavioural responses in fish [61], indicating that these short-term exposures to elevated CO$_2$ have not produced adaptations that overcome longer term exposure to elevated pCO$_2$.

Unlike most marine systems, fluctuations in pCO$_2$ may occur for extended periods (e.g. weeks to months) in some freshwater systems. In large rivers and lakes, O$_2$ saturation may naturally range from anoxia to super-saturation as a result of seasonal phenomena [113,114]. Environmental hypercapnia is common in some freshwater systems, with the most extreme examples being tropical aquatic environments [115]. Many freshwater fish have become tolerant to these O$_2$ fluctuations. In highly productive systems in which CO$_2$ and O$_2$ are usually inversely related [116], it is likely that they may also have become tolerant to high CO$_2$. Thus, if freshwater fish can tolerate periods of lower O$_2$ tension than most marine fishes, then they may also have become more tolerant to higher pCO$_2$ tension [117]. Although complete or significant degrees of physiological pH compensation during hypercapnia have been demonstrated in both freshwater and marine fish species [118–120], freshwater fishes were shown to have adapted to the most extreme conditions [117]. Therefore, compared with marine ecosystems, the extended periods of pH and pCO$_2$ shifts occurring in freshwater may have set the stage for greater tolerance of
freshwater fish towards acidification and reduced their susceptibility to rising atmospheric CO2. Interestingly, significant interspecific differences in the sensitivity of reef fishes to CO2-induced acidification exist [67]. Thus, not all species will be affected in the same way by acidification, probably resulting in shifts in assemblage structure favouring more tolerant species.

6. Management implications and conclusions

Considering that species and ecosystem-specific differences exist in olfactory-mediated responses of fish to acidification, understanding these critical dissimilarities becomes important for dealing with the ecological consequences of near-future acidification in freshwater and marine systems. Management strategies in a high CO2 world are clearly dissimilar between freshwater and marine ecosystems. In freshwater, short-term (and local) mitigations of the effects of acidification may include the liming of rivers or lakes. This technique by which ambient acidified water pH may be partially neutralized has been extensively and successfully used in Scandinavia [121]. Furthermore, emissions of sulfur dioxides and nitrogen oxides, which drive freshwater acidification, can be curtailed over relatively short timeframes (e.g. years to decades), as evidenced by the success in reducing these atmospheric pollutants in Northern America and Europe [13]. Consequently, there are local and regional management strategies that can be used to help combat the impacts of freshwater acidification. Within freshwater ecosystems, hatchery-reared fishes are commonly stocked into natural waterways as part of population recovery and maintenance programmes. Recent work suggests that the survival of hatchery-reared fishes may be lower than that of natural populations [122], partly owing to their inability to respond to natural predators. This naivety to novel predators could be compounded if hatchery-reared fishes are stocked into weakly acidic conditions, under which the ability to rely on innately aversive chemical alarm cues is reduced [24,42]. Hence, ambient pH or the timing of episodic acidification events should be included as a variable in stocking efforts to minimize such predator advantage [123].

By contrast, for marine ecosystems no local solution exists to temper the effects of acidification on the behavioural impairment observed in fishes. A strategy of globally limiting atmospheric CO2 increase is at present the only solution to ocean acidification, from which freshwater ecosystems would also benefit following reductions in the severity of acid rain [7]. A major concern is that atmospheric CO2 levels are set to exceed 500 ppm by 2050 and are on track to reach at least 900 ppm by 2100 [17,58]. Consequently, in the second half of this century, the surface ocean will experience CO2 levels that are known to significantly impair the behaviour of some marine fishes, unless significant and sustained reductions in global CO2 emission are achieved. Given the significant interspecific differences in the sensitivity of reef fishes to CO2-induced acidification [67], not all species will be affected the same way by future ocean acidification, probably resulting in shifts in community structure favouring more tolerant species. Further tests on species-specific response to acidification will be necessary for managers to predict which species might be at greatest risk and concentrate conservation efforts on these species. Limiting other stressors and impacts, for instance fishing mortality, may be one way to help maintain viable populations of sensitive species and to reduce the impacts of acidification on assemblage structure and ecosystem function.

A major unknown in predicting the future impacts of acidification, in both freshwater and marine ecosystems, is the capacity for adaptation to lower pH and/or higher pCO2. The different mechanisms of impaired olfactory-mediated behaviour in freshwater (e.g. degradation of chemosensory molecules, reduced olfactory/chemosensory sensitivity) and in marine (e.g. altered neurotransmitter function) fishes (and potentially in invertebrates) might lead to different prospects for adaptation. Little is known regarding the potential of freshwater fishes’ olfactory systems to adapt to the loss of relevant chemical cues in low pH water. It is possible that there could be selection favouring individuals that respond most strongly to low levels of olfactory cues; however, other sensory modalities (i.e. vision) may also play a heightened role if chemical cues become deactivated [38,48]. In marine habitats, adaptation through selection on individual variation in CO2 sensitivity could occur. Variation in the level of behavioural impairment exhibited by individual reef fishes exposed to elevated pCO2 has been observed in some studies, with some individuals apparently more resistant to the effects of elevated CO2 than others [61]. Furthermore, natural selection favouring CO2 tolerant individuals has recently been demonstrated under natural conditions [111]. Consequently, there is clearly the potential for natural variation in sensitivity among individuals to lead to genetic adaptation in marine fishes. Understanding the adaptive potential of marine fishes to elevated CO2 and the speed at which adaptation might occur will be critical in predicting the impacts of acidification on marine ecosystems. Ultimately, an evolutionary perspective will be required to assess the likely ecosystem effects of acidification in both freshwater and marine ecosystems.

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