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Experimental validation of a time-dependent model for chemical taste taint accumulation as geosmin (GSM) and 2-methylisoborneol (MIB) in commercial RAS farmed barramundi (*Lates calcarifer*)

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A B S T R A C T

The accumulation of naturally-derived taste taint chemicals, geosmin (GSM) and 2-methylisoborneol (MIB), impair the flavour of Recirculating Aquaculture System (RAS) farmed-fish. Quantification and control of these by analytical or sensory means are not presently practical for RAS farmers. To forecast taste taint in RAS, a time-dependent model was synthesised (Ecological Modelling 291 (2014) 242–249). Here we report for the first time an extensive two-year validation study of this model with commercial RAS farmed barramundi (*Lates calcarifer*) in which fingerlings (~0.01 kg) were grown to harvest (~0.85 kg) at 245 days. The concentration of GSM and MIB in the growth water and fish-flesh was determined (weekly) using Headspace Solid-Phase Micro-Extraction, followed by Gas Chromatography Mass-Spectroscopy (and microwave-mediated distillation). The concentration of both taint chemicals in the RAS growth water was controlled using continuous dosing of hydrogen peroxide (2.5 mg L^{-1}) as a benign biocide. A special dosing apparatus was developed for this purpose. Results showed, generally, very good agreement between observed and predicted taint values in the range 0–2 μg kg^{-1}, and especially below the important consumer rejection threshold (<~0.7 μg kg^{-1}). A minor anomaly was a general over-prediction of chemical in about a half of the $N = 706$ simulations in the range 0–12 μg kg^{-1}. Predictions were conservative therefore i.e. on the 'safe' side. This is attributed, largely, to dissimilar (exponential) growth constant (γ) for smaller and larger fish, and the fact that the RAS environment is oscillatory. Findings highlight that the work could be meaningfully applied to RAS systems to develop protocols to limit taste taint in harvested fish. Significantly, these results are the first for RAS farmed-fish covering an entire production cycle from fingerlings to harvest. The work will be of immediate benefit and interest to RAS farmers, selling agents and researchers.

1. Introduction

Farming of fish in Recirculating Aquaculture Systems (RAS) is becoming widespread to fill the demand gap due to diminishing wild-caught supplies. Barramundi (*Lates calcarifer*) is grown as an RAS farmed-fish because of high demand as a premium food.

However, the natural accumulation in RAS fish-flesh of 'earthy' or 'muddy' off-flavours due to taint accumulation of chemicals as geosmin (GSM) or 2-methylisoborneol (MIB) is a major concern. Inconsistent taste quality of farmed barramundi has been identified as a major issue in buyer resistance.

A number of approaches to remove or inactivate these taste taint chemicals have been investigated – but effective practices to control taste taint have not gained acceptance (Howgate, 2004; Schrader et al., 2010). Presently, barramundi farmers rely on post-harvest purging with clean water as a taste taint abatement strategy. However, a drawback is fish are not fed during this purge-stage and lose mass (weight), resulting in a financial penalty (Palmeri et al., 2008).

The consumer rejection threshold concentration for these taste taint chemicals in RAS fish-flesh is ~0.7 μg kg^{-1} (Robertson et al., 2005). Fish exceeding this threshold concentration are regarded as un-marketable. The limiting concentration of GSM and MIB in the RAS growth water that will impart this level of unwanted off-flavour to the harvested fish-flesh is 0.015 and 0018 μg L^{-1} respectively (Persson and York, 1978; Persson, 1980). That is, where the concentration in the growth water of the taint chemical exceeds

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Nomenclature

a	Taint elimination coefficient, day^{-1} (5)
b	taint accumulation coefficient, $\mu g\,kg^{-1}\,day^{-1}$ (4)
C_{OX}	concentration of dissolved oxygen, $mg\,L^{-1}$ (12)
C_W	Taint concentration (as GSM or MIB) in water, $\mu g\,L^{-1}$ (2)
$\frac{dy}{dt}$	Rate of change of taint in fish-flesh, $\mu g\,kg^{-1}\,day^{-1}$ (1)
e	Lipid mass ratio, dimensionless fraction (16)
E_W	Chemical uptake efficiency across the gill, dimensionless fraction (9)
GSM	Geosmin
G_V	Gill ventilation rate, $l\,day^{-1}$ (9)
k_1	Taint accumulation through gills, $l\,kg^{-1}\,day^{-1}$ (2)
k_2	Taint elimination through gills, day^{-1} (2)
k_g	Growth dilution plus metabolic transformation, day^{-1} (2)
k_G	Rate constant for growth dilution, day^{-1} (17)
k_m	Rate constant for metabolic transformation, day^{-1} (17)
K_{OW}	Octanol- water partition coefficient, dimensionless (10)
m_f	Mass of the fish at t, kg (2)
MIB	2-methylisoborneol
n	Number of data
N	Number of all data
Q_W	Rate of chemical transport in the aqueous phase, $l\,day^{-1}$ (13)
Q_L	Rate of chemical transport in the lipid phase, $l\,day^{-1}$ (13)
RAS	Recirculating aquaculture system
R^2	Correlation coefficient
T	temperature, °C (12)
t	Growth time, day (1)
V_L	Lipid mass (weight), kg (13)
y	Taint (as GSM or MIB) concentration, $\mu g\,kg^{-1}$ (1)

Greek symbols

β	Pre-exponential growth constant, kg (3)
γ	Exponential growth constant, day^{-1} (3)

this limiting value, the fish-flesh will consequently become unacceptably tainted.

A major difficulty is quantification of GSM and MIB taste taint chemicals in RAS water and fish-flesh because of the costs involved, experimental time and the few research institutes that have the necessary facilities (G. Vandenberg, Faculté des sciences de l'agriculture et de l'alimentation, Université Laval, *pers. comm.*). As an alternative, sensory (taste and smell) assessments have been adopted to determine whether a fish is tainted beyond a threshold (Grimm et al., 2004; Percival et al., 2008). This approach however is based on human perception and requires 'experts' to do this accurately. It is therefore subjective, and; it is questionable whether the experts are representative of the consumer population (Howgate, 2004). Moreover, it is suggested, successive testing of MIB, for example, influences the taste adaptation in experts that can lead to a reduction in sensitivity to taste taint (Brett and Johnsen, 1996; Johnsen and Brett, 1996). Both approaches therefore are not practical or feasible for use by farmers and farming management during RAS fish growth.

Predictive models, widely used in chemical and bio-chemical engineering however, provide a quantitative basis for evaluating toxicology and risk assessments in fish. An adequate model could be used to predict taste taint in fish-flesh with time and assist farmers to harvest fish with taste taint lower than the rejection threshold. This has led to a number of modelling approaches. Until recently however these models were based on assumptions of steady-state.

Because there was no evidence to show that net chemical exchange was in fact zero across the RAS water phase and fish body, Hathurusingha and Davey (2014) synthesised a quantitative model that predicted the time-dependent concentration of taste taint chemicals as GSM and MIB in RAS fish-flesh. The model was based on conservation of mass and energy, and thermodynamic processes established in bio-chemical engineering. Chemical uptake and elimination routes into and from the fish were integrated. The model was illustrated with independent (but fragmented) literature data for farmed barramundi

($n \geq 14$). The applicability of a generalized form of the model to other aquaculture species, in particular rainbow trout (*Oncorhynchus mykiss*), was demonstrated with independent data ($n \geq 15$) (Davey and Hathurusingha, 2014; Hathurusingha and Davey, 2013).

There has been however no detailed study reported (or as far as can be determined even undertaken) to analyse GSM and MIB in RAS growth water and accumulated concentrations in fish-flesh of barramundi, especially covering an entire commercial production cycle (245 days). This gap emphasized the need for an extensive and dedicated sampling of the RAS growth water and fish-flesh for the model validation.

1.1. This study

Here, the model of Hathurusingha and Davey (2014) is experimentally tested against extensive and original data obtained from commercial-scale RAS farmed barramundi from fingerlings (~0.01 kg) to harvested fish (~0.85 kg) for the first time.

Both GSM and MIB in growth water and barramundi fish-flesh were sampled weekly. A number of experimental and analytical protocols were expressly adapted for this purpose. The concentration of taint chemicals in the RAS growth water was controlled using continuous dosing of hydrogen peroxide ($2.5\,mg\,L^{-1}$) as a benign biocide via a specially-developed apparatus. This consisted of a controller, H_2O_2 sensor (*ProMinent Fluid Controls Pty Ltd,* Germany) and a metering pump (*Global Pumps Pty Ltd,* Australia). It was operated automatically in an on/off mode in which dosing of H_2O_2 to the growth water was cut off when the bulk water residual concentration reached a set-point. Dosing resumed when the concentration dropped below the set-point. The apparatus and its safe and Standard Operating Procedures (SOPs) are described in detail in Hathurusingha (2015). Further, this study is the first full-scale experimental investigation of the accumulation of GSM and MIB in any RAS fish species. Rigorous analyses of observed against predicted taste taint data are presented. Results are discussed with a view to development of RAS growth protocols to limit GSM and MIB in the flesh of fish.

Findings will be of immediate benefit and interest to RAS farmers, selling agents and researchers.

2. Materials and methods

2.1. Model for taste taint

The transient model for chemical taste taint accumulation of Hathurusingha and Davey (2014) can be summarised as follows: The governing route for taste taint uptake into the fish-flesh is assumed to be the gills, and elimination, from the gills, bio-transformation and fish growth dilution. The optimum growth-temperature of the RAS water for barramundi is considered to be 28 °C.