Environmental Pollution 158 (2010) 1809–1816

Contents lists available at ScienceDirect

Environmental Pollution

journal homepage: www.elsevier.com/locate/envpol

Environmental and human health risk assessment of organic micro-pollutants occurring in a Spanish marine fish farm

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Exposure and effects of twelve organic micro-pollutants are evaluated at a Spanish fish farm.

ARTICLE INFO

Article history:
Received 14 May 2009
Received in revised form
30 September 2009
Accepted 5 November 2009

Keywords:
Aquaculture
Ecological risk assessment
Health risk assessment
Secondary poisoning
Irgarol 1051

ABSTRACT

In this work the risk posed to seawater organisms, predators and humans is assessed, as a consequence of exposure to 12 organic micro-pollutants, namely metronidazole, trimethoprim, erythromycin, simazine, flumequine, carbaryl, atrazine, diuron, terbutryn, irgarol, diphenyl sulphone (DPS) and 2-thiocyanomethylthiobenzothiazole (TCMTB). The risk assessment study is based on a 1-year monitoring study at a Spanish marine fish farm, involving passive sampling techniques. The results showed that the risk threshold for irgarol concerning seawater organisms is exceeded. On the other hand, the risk to predators and especially humans through consumption of fish is very low, due to the low bioconcentration potential of the substances assessed.

1. Introduction

Aquaculture is the farming of aquatic organisms including fish, molluscs, crustaceans and aquatic plants, using techniques designed to increase the productivity of these organisms beyond the natural capacity of the environment. Intensive aquaculture is commonly practised in cages or ponds: involving the control of breeding, and supply of artificial feed and medication. The increase in demand for seafood and the decline in world fisheries have contributed to an unprecedented growth in this industry over recent decades. As a result, it is growing more rapidly than any other animal food-producing sector in the world (Nierentz, 2007). Aquaculture production in 2005 (excluding plants) was reported as being 48.1 million tonnes, which represents 45% of the global seafood supply and is valued at 70.9 US$ billion in value (Nierentz, 2007). Unfortunately, the sustainability of intensive aquaculture has been brought into question, due to its potential environmental impacts, including pressure on feed resources (Naylor et al., 2000), destruction of mangroves and wetlands (Paez-Osuna, 2001), discharge of particulate and dissolved organic matter through faeces and feed wastage (Read and Fernandes, 2003), eutrophication (Folke et al., 1994; Loya et al., 2004), genetic interaction between escaped and wild fish (Youngson et al., 2001), disease transfer to wild fish (Heggberget et al., 1993) and human health risks due to accumulation of persistent organic pollutants in farmed fish (Hites et al., 2004). Another key impact of intensive aquaculture is the dispersion of chemicals in the environment (Gräslund and Bengtsson, 2001), such as disinfectants, antifoulants and veterinary medicines. These chemicals are essential for aquaculture in order to increase and control production of seed in hatcheries, increase feeding efficiency, improve survival rates, control pathogens and diseases and reduce transport stress (Huntington et al., 2006). However, the aquaculture industry has adopted the use of chemicals originally developed for other sectors, especially agriculture. Many chemicals now in common use in aquaculture have never been evaluated in the context of their effects on the aquatic environment, particularly coastal waters (Huntington et al., 2006). One of the reasons for this is the lack of reliable analytical data in seawater, as a consequence of the difficulties in detecting organic pollutants in this medium, such as the complexity of the matrix, the high dilution factor or degradation phenomena (Pouliquen et al., 2007). For this reason, the environmental assessment of chemicals in the marine environment requires the development of highly-specific and sensitive analytical procedures, allowing us to detect pollutant concentrations below ng L^{-1} or pg L^{-1}.

From October 2005 to October 2006 a micro-pollutant monitoring campaign was carried out in a fish farm located in south-eastern Spain, where sea bream (*Sparus aurata*) and sea bass (*Dicentrarchus labrax*) are farmed. Instead of traditional water

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doi:10.1016/j.envpol.2009.11.006

sampling methods, passive sampling methods were used, namely Polar Organic Chemical Integrative Samplers (POCIS) (Álvarez et al., 2004). Target substances included 23 organic chemicals belonging to different groups: antibiotics, fungicides, herbicides and biocides. It must be stressed that the particular products used in the farm were not disclosed by the company. Hence, the target substances were selected on the basis of being commonly used in aquaculture. 12 substances were detected during the one-year campaign: metronidazole, trimethoprim, erythromycin, simazine, flumequine, carbaryl, atrazine, diuron, terbutryn, irgarol, diphenyl sulphone (DPS) and 2-thiocyanomethylthiobenzothiazole (TCMTB). In this paper we assess by means of Risk Assessment the toxicological risks to the marine aquatic environment and to human health posed by these chemicals. Further details on the micro-pollutant monitoring campaign can be found in Martínez-Bueno et al. (2009).

2. Risk assessment methodology

The Risk Assessment of chemicals has been carried out using the European Commission's Technical Guidance Document on Risk Assessment (TGDRA) (EC, 2003) as the methodological reference.

2.1. Protection goals

Risks addressed by this paper are those related to toxic effects in the environment and in humans. The areas of protection for which risk is assessed are the following:

- Seawater organisms
- Seawater (fish-eating) predators
- Humans, through fish consumption

Protecting marine sediment-dwelling organisms is also relevant in this context; however, the monitoring campaign in the fish farm did not include sediment analyses. In addition, experimental toxicity data on sediment organisms is scarce. For this reason, the environmental risk on sediments is only discussed qualitatively.

2.2. Target substances

The substances subject to the risk assessment are those which were detected in the monitoring campaign (Table 1). All these substances are assessed in terms of risk to seawater organisms, predators and humans upon consumption of fishery products. It must be highlighted that the actual chemicals used in the farm were not disclosed. Therefore, the list of target pollutants could be incomplete.

2.3. Exposure assessment

The goal of the exposure assessment is to estimate the predicted environmental concentrations or doses to which organisms in ecosystems and humans will be exposed. The assessment is based on the calculations proposed by the TGDRA (European Commission, 2003) and the European Uniform System for the Evaluation of Substances (EUSES) (European Commission, 2004).

Predicted environmental concentrations in seawater (PEC_{seaw}, in mg L^{-1}) have been obtained from the analytical results of the monitoring campaign (Table 1). PEC_{seaw} corresponds to the yearly average concentration, calculated as the average from the 12 samples. When a substance was not detected in a sample, the concentration taken into account for that sample was zero.

The predicted concentration in fish (C_{fish}, in mg kg_{wwt}^{-1}) is calculated following the TGDRA guidelines, using eq. (1):

$$C_{fish} = PEC_{seaw} \times BCF_{fish} \times BMF_{fish} \quad (1)$$

where BCF_{fish} is the bioconcentration factor in fish (L kg_{wwt}^{-1}) and BMF_{fish} is the biomagnification factor in fish (dimensionless). Values for BCF_{fish} (Table 2) have been obtained from published experimental measures, or in the absence of the latter, by means of the BCFWIN program (Meylan et al., 1999). BMF_{fish} has been estimated using the semi-quantitative approach suggested in the TGDRA (part II, Table 21), which assigns values in the 1–10 range, based on the magnitudes of log Kow and BCF_{fish}. For all the substances in our case study, the obtained BMF_{fish} is 1.

The predicted human dose via consumption of farmed fish (PHD, in mg kg_{bw}^{-1} d^{-1}) is calculated using eq. (2):

$$PHD = \frac{C_{fish} \times IH_{fish}}{BW} \quad (2)$$

where IH_{fish} is the fish intake (kg $person^{-1}$ d^{-1}) and BW is the body weight, assumed to be 70 kg (European Commission, 2004). The average finfish consumption in Spain (including fresh, frozen and canned fish) is 0.07 kg $person^{-1}$ d^{-1} (Ministerio de Agricultura, Pesca y Alimentación, 2006). Using eq. (2), with the data mentioned constitutes a worst-case approach, since it is assumed that the consumer's whole finfish diet consists of sea bass/sea bream, and that the latter originates exclusively from the studied farm. In Table 3 the predicted concentrations and doses calculated with eqs. (1) and (2) are summarised.

Table 1
Analytical results obtained during a 1-year monitoring campaign at the fish farm.

Group	Compound	Positive samples ($n = 12$)[a]	Concentration range in positive samples (ng L^{-1})[a]	PEC_{seaw} (ng L^{-1})[b]
Antibiotics	Ciprofloxacin	n.d	–	–
	Enrofloxacin	n.d	–	–
	Erythromycin	5	0.01–0.03	0.0073
	Flumequine	1	0.13	0.011
	Mepivacaine	n.d	–	–
	Metronidazole	1	13.4	1.12
	Oxolinic acid	n.d	–	–
	Oxytetracycline	n.d	–	–
	Sulfamethoxazole	n.d	–	–
	Tetracycline	n.d	–	–
	Trimethoprim	1	0.23	0.02
Herbicides	Albendazole	n.d	–	–
	Atrazine	12	0.2–1.5	0.85
	Carbaryl	1	4.50	0.38
	Dichlorvos	n.d	–	–
	Diflubenzuron	n.d	–	–
	Diphenyl sulphone, DPS	12	15.5–75.6	45.55
	Diuron	5	0.4–2.5	1.45
	Simazine	12	0.1–0.9	0.95
	Terbutryn	10	0.02–0.1	0.06
Fungicides	Malachite green	n.d	–	–
Biocides	Irgarol	12	0.02–0.7	0.36
	TCMTB	1	3.10	0.26

n.d.: not detected.
[a] Martínez-Bueno et al. (2009).
[b] Calculated as a yearly average. Zero was used as the concentration in samples were the compound was not detected.

2.4. Effects assessment

Effects assessment concerns the hazard identification and dose-response assessment of toxicological and ecotoxicological data. In ecotoxicological effects assessment, the predicted no-effect concentrations (PNECs) are derived from experimental toxicity data using assessment factors. In human toxicological effects assessment, a human reference dose (HRD) is derived from the available data.

The predicted no-effect concentration for seawater organisms ($PNEC_{seaw}$) has been obtained for most substances by means of single-species ecotoxicity data from tests with seawater and/or freshwater organisms, and the application of assessment factors. Most of the references used for aquatic ecotoxicity, either from seawater or freshwater, were retrieved from the USEPA Ecotox database (USEPA, 2009a), although in the particular case of DPS – due to the lack of experimental toxicity values to complete the minimum dataset (fish, crustaceans and algae) – values from the ECOSAR software were used (USEPA, 2009b). Concerning assessment factors, these were chosen depending on the number and the quality of the ecotoxicity data available, as suggested by the TGDRA (part II, Table 25).

On the other hand, the pesticides simazine, atrazine and diuron are priority substances classified in the European Water Framework Directive (European Parliament, 2000), for which environmental quality standards (EQS) have recently been approved through the Directive on Priority Substances (European Parliament, 2008). For these three substances, the corresponding EQS have been used as $PNEC_{seaw}$, since they were determined following risk assessment methods and according to the Water Framework Directive EQS applied for coastal waters.

Concerning secondary poisoning, the concentration of chemicals in food for predators should be below the predicted no-effect concentration for predators ($PNEC_{oral}$) in a (sub)chronic dietary toxicity test with animals representative of fish-eating birds or mammals. $PNEC_{oral}$ is calculated from a non-observed effect concentration (NOEC) in food and assessment factors are set by the TGDRA (part II, Table 23). In the absence of a NOEC, the non-observed effect level (NOAEL) for mammals or birds can be converted into a NOEC in food by means of appropriate conversion factors provided by the TGDRA (part II, eqs. 77 and 78). For metronidazole, trimethoprim, erythromycin and DPS, it was not possible to find NOEC or