Ullrich, S., Tanton, T., Abdrashitova, S., 2001. Mercury in the environment: a review of the factors affecting methylation. Critical Reviews in Environmental Science and Technology 31 (3), 241–293.

Vazquez, G.F., Reyes, M.C., Fernandez, G., Aguayo, J.E.C., Sharma, V.K., 1997. Contamination in marine turtle (*Dermochelys coriaca*) egg shells of Playon de Mexiquillo, Michoacan, Mexico. Bulletin of Environmental Contamination and Toxicology 58 (2), 326–333.

Villaescusa, C., Gutierrez, E., Flores, G., Arreola, M., 1991. Metales traza en el mejillon, Modiolus capax, del Golfo de California: variaciones geograficas. Congreso de la Asociacion de Investigadores del Mar de Cortes, 17.

Waldichuck, M., 1987. Natural versus anthropogenic impacts. Marine Pollution Bulletin 18 (4), 143–144.

0025-326X/$ - see front matter
doi:10.1016/j.marpolbul.2006.09.019

Copper emission factors from intensive shrimp aquaculture

L.D. Lacerda [*,1], J.A. Santos, R.M. Madrid

Instituto de Ciências do Mar, Universidade Federal do Ceará, Av. Abolição 3207, Fortaleza, CE, Brazil

Emission factors, i.e., the amount of a given pollutant emitted per unit of production goods or production area, are strong tools for estimating pollutant loads to the environment from a variety of anthropogenic sources, since they can derive a difficult measurable variable (pollutant load) from an easily assessed parameter (e.g., area, amount of goods produced, inhabitants) and have been successfully used at the global (e.g., Nriagu and Pacyna, 1988); regional (e.g., Hutton and Symon, 1986) and local level (e.g., Molisani et al., 2004; Lacerda et al., 2006), to estimate pollutant emissions from natural and anthropogenic sources to the environment. Emission factors are also presently used in most countries' environmental agencies to create and update pollutant inventories statistics (e.g., EEA, 1999; EPA, 2002; Molisani et al., 2004).

The fast growth of intensive shrimp farming worldwide and its dependence on large inputs of artificial feed, fertilizers and of other chemical addictives such as acidity correctors and algaecides have triggered many studies to investigate shrimp farm's role as nutrient sources to coastal environments which allowed the calculation of emission factors for major nutrients such as N and P (Páez-Ozuna et al., 2003; Burford et al., 2003).

Trace metals, however, are not obvious pollutants present in shrimp farm effluents. However, some trace metals are present as natural components in aquafeeds, as impurities in fertilizers or as active principles of pesticides (Boyd and Massaut, 1999; Tacon and Forster, 2003). But since shrimp farming is generally developed in areas without significant sources of trace metals, their emissions can be relatively important for these regions. Among the trace metals eventually present in shrimp farm effluents, Cu is of high significance not only due to its ubiquitous presence in aquafeeds and other chemicals and to its toxicity to phytoplankton and the shrimps proper (Bainy, 2000; Chen and Lin, 2001; Lee and Shiau, 2002).

Shrimp farming in NE Brazil has increased exponentially during the past 10 years from an annual production of about 7000 tons, produced in less that 1000 ha of pond area in 1998 to over 90000 tons produced in about 15000 ha of pond area in 2003 (Madrid, 2004). This resulted in an increase in nutrient emissions to estuaries in many areas, which formerly had no significant pollution sources. A previous survey of trace metal content in shrimp and aquafeeds performed in some major farms in this area showed relatively high concentrations of Cu and suggested deleterious effects of this trace metal on shrimp productivity (Lacerda et al., 2004). In the present study we present the first estimate of Cu emission factor from intensive shrimp farming based on experimental data from a typical farm in Northeastern Brazil. The high similarity of emission factors for N and P from these farms and their technological processes with those generated from farms in Mexico and Australia (Páez-Ozuna et al., 2003; Burford et al., 2003; Jackson et al., 2003; Lacerda et al., 2006), suggests that the proposed emission factor for Cu may be applied for the shrimp farming industry worldwide.

Copper emission factor was generated by analyzing Cu concentrations in aquafeeds and other chemical addictives, in shrimp biomass and in inflow and outflow water and suspended particles and in pond bottom sediments of the largest shrimp farm of Ceará State NE Brazil, located at the Jaguaribe River estuary, latitude 4°23′ S and longitude 37°36′ W. Table 1 shows the major production parameters of the farm used in the calculation of the emission factor. These parameters are typical of intensive shrimp farming in Brazil and similar to those verified in shrimp farming worldwide.

Samples for Cu determination were collected during one production cycle using clean procedures. Water samples in the inflow canal, inside two ponds and in the outflow canal

---

[*] Corresponding author. Tel.: +55 85 324421263; fax: +55 85 32683205. *E-mail address:* pgcmt@labomar.ufc.br (L.D. Lacerda).

[1] On leave from Departamento de Geoquímica, Universidade Federal Fluminense, Niterói, 24020-0-7 RJ, Brazil.

Table 1
Management characteristics of the studied shrimp farm at the Jaguaribe River estuary, NE Brazil

Parameter	Dimension
Pond size	3.2 ha
Pond depth	1.5 m
Water management	First 30 days without renewal. 5% daily volume renewal onwards
Growth cycles per year	2.3
Approximate growth period	135 days
Shrimp production	4540 kg ha^{-1} cycle^{-1}
Aquafeeds consumption	7940 kg ha^{-1} cycle^{-1}
Lime application	2370 kg ha^{-1} cycle^{-1}
Fertilizer application	46 kg ha^{-1} cycle^{-1}

were collected using pre-cleaned 1.5 L PET bottles. Samples were filtered non-longer than 3 h from collecting through acid-cleaned cellulose acetate filter with 0.45 μ of pore diameter for the collection of total suspended solids. Bottom sediments were sampled by hand directly in pre-cleaned plastic bags in different sites of the two ponds. During the growth cycle shrimps were sampled monthly and separated in muscle tissue and exoskeleton for analysis. Sediments and shrimps were kept frozen till analysis. Samples of 15 brands of aquafeeds, fertilizers and other chemical addictives used in the Jaguaribe Estuary shrimp farms were also analyzed. All solid samples were oven-dried to constant weight and ashed (450 °C/24 h) to remove the organic matter.

Filtered water samples were acidified and UV-treated to release Cu from strong organic complexes. Cu concentrations were determined by graphite furnace atomic absorption spectrophotometry. Ashes from solid samples were digested in 20 mL of 50% *aqua regia* solution for 2 h in Teflon crucibles at 80 °C. Simultaneously standard reference material NIST 2976 (mollusk tissue) and NIST 1646a (estuarine sediments) were treated similarly. The acid extracts were analyzed by conventional flame atomic absorption spectrophotometry in a Shimadzu AA-6200 spectrophotometer. Table 2 shows the comparison between certified and measured concentrations showing good recuperation of the certified concentrations, 92% for mollusk tissue and 88% for estuarine sediments.

Different aquafeed brands used in the studied farm showed average Cu concentrations ranging from 13.1 to 79.0 μg g^{-1} d.w. Concentrations in fertilizers varied from 0.7 to 2.0 μg g^{-1} d.w., whereas in other chemicals (lime and chloride) Cu concentrations varied from 1.9 to 3.3 μg g^{-1} d.w. (Table 3). Aquafeeds are by far the largest contributor of Cu to shrimp ponds due to the higher Cu concentrations and the larger amount used.

Table 2
Comparison between Cu concentrations (μg g^{-1} d.w.), mean and standard deviation, in certified reference samples (National Institute of Standards & Technology – NIST) with those analyzed in the present study

Standard	*n*	Certified value	Measured value
NIST 1646a Estuarine Sediment	6	10.01 ± 0,34	8.8 ± 0.1
NIST 2976 Mollusk tissue	6	4.02 ± 0,33	3.7 ± 0.6

Table 3
Copper concentrations (μg g^{-1} d.w., mean and standard deviation) in different brands of aquafeed*, fertilizers and other chemicals frequently in use by the studied farm

Substance	*n*	Cu
Dolomite lime	4	3.3 ± 0.2
Dolomite lime	4	1.9 ± 0.1
Granulated Chloride	3	3.3 ± 0.3
NutriLake (Fertilizer)	5	0.7 ± 0.3
Super phosphate	5	2.0 ± 0.2
Aquafeed 01	5	34.3 ± 0.8
Aquafeed 02	5	13.1 ± 1.0
Aquafeed 03	5	47.8 ± 0.1
Aquafeed 04	5	79.0 ± 5.0
Aquafeed 05	5	51.9 ± 0.1
Aquafeed 06	5	51.9 ± 1.3
Aquafeed 07	5	44.6 ± 0.1
Aquafeed 08	5	50.5 ± 2.4
Aquafeed 09	5	51.0 ± 13.5
Aquafeed 10	5	41.0 ± 15.1

*Since we are not a certified official laboratory we are not allowed to give the names of brands analyzed.

Suspended particulate matter (TSS) was higher (80–164 mg L^{-1}) in input waters than in pond waters (62 mg L^{-1}) and also higher than in renewal waters (87 mg L^{-1}). Extremely high TSS content was determined in bottom draining waters (1675 mg L^{-1}), a 19-times increase relative to surface waters. This suggests that at the end of the cycle when the pond is emptied, water currents moving into the central draining canal may be strong enough to erode and transport at least the surface nefloid layer of bottom sediments. Figueiredo et al. (2005) analyzing TSS balance in another farm at the Jaguaribe River using a similar cultivation processes found a 17-times TSS increase in bottom waters relative to surface waters. These authors monitored the emptying process and found that TSS-enriched waters represents about 20% of the total pond volume.

Copper concentrations in all analyzed samples are presented in Table 4. Average dissolved Cu concentrations were similar between input (7.2 μg L^{-1}) and output water (6.9–7.2 μg L^{-1}), resulting in no statistically significant net export of dissolved Cu to adjacent mangrove waters. Particulate Cu concentrations were higher in input waters (3.7–9.5 μg L^{-1}) than in pond (2.6–3.3 μg L^{-1}) and renewal output water (3.0–3.3 μg L^{-1}). However, the high TSS content of draining output water resulted in much higher particulate Cu concentrations (114 μg L^{-1}) resulting in a net export of particulate Cu of about 168 g ha^{-1} cycle^{-1}. This behavior is similarly to N and P behavior reported in other studies (Figueiredo et al., 2005), and represents the major form of Cu export from the ponds. Nutrients, in particular N and P export from shrimp farming is (∼60% and >98% for N and P, respectively) constituted by particulate forms mostly released during the end of the draining process

Table 4
Copper concentrations (μg g^{-1} d.w. for solid samples and μg L^{-1} for waters), mean and standard deviation and average input and outputs loads (g ha^{-1} cycle^{-1}) in samples collected from an intensive shrimp farm at the Jaguaribe estuary, NE Brazil: (+) added to system; (−) lost from system

Sample	Cu concentrations	Average Cu loads
Input filling water, dissolved[a]	7.2 ± 0.4	+108 ± 6
Input filling water, particulate[b]	9.5 ± 0.6	+143 ± 9
Input replacing water, dissolved[c]	7.2 ± 0.4	+57 ± 3
Input replacing water, particulate[d]	9.5 ± 0.6	+75 ± 5
Average total Cu input from waters	–	***+383***
Input from aquafeeds	34–52	+188
Input from fertilizers	0.7–1.9	+0.6
Input from lime	1.9–3.2	+5.9
Average total Cu input from chemicals	–	***+194.5***
Average total Cu input		**+577.5**
Output renewal water, dissolved[e]	7.2 ± 0.5	−46 ± 4
Output renewal water, particulate[f]	3.0 ± 0.6	−24 ± 2
Output draining effluent water, dissolved[g]	6.9 ± 0.3	−99 ± 4
Output draining effluent water, particulate		
Surface waters 80% of total volume[h]	3.3 ± 0.6	−40 ± 7
Bottom waters 20% of total volume[i]	114 ± 17	−342 ± 51
Average total Cu output from waters	–	***−551***
Excess Cu exported through waters[j]		***−168***
Average Cu loss through shrimp biomass	***37–47***	***−12.8***
Cu available for sedimentation[k]	–	**+13.7**

[a] Pond volume: 4.8×10^7 L × dissolved Cu (μg L^{-1}) in input water × 3.2 ha^{-1}.

[b] Pond volume: 4.8×10^7 L × particulate Cu (μg L^{-1}) in input water × 3.2 ha^{-1}.

[c] First 30 days without replacing: 0.5% of pound volume per day: 0.024×10^7 L × 105 days × dissolved Cu (μg L^{-1}) in input water × 3.2 ha^{-1}.

[d] First 30 days without replacing: 0.5% of pound volume per day: 0.024×10^7 L × 105 days × particulate Cu (μg L^{-1}) in input water × 3.2 ha^{-1}.

[e] First 30 days without replacing: 0.4% of pound volume per day: 0.024×10^7 L × 105 days × dissolved Cu (μg L^{-1}) in average pond water × 3.2 ha^{-1}.

[f] First 30 days without replacing: 0.4% of pound volume per day: 0.024×10^7 L × 105 days × particulate Cu (μg L^{-1}) in average pond water × 3.2 ha^{-1}.

[g] Pond volume × 0.8: 4.8×10^7 L × particulate Cu (μg L^{-1}) in surface output water × 3.2 ha^{-1}.

[h] Pond volume × 0.2: 4.8×10^7 L × particulate Cu (μg L^{-1}) in bottom output water × 3.2 ha^{-1}.

[i] Input through water minus output through water.

[j] Input through water minus output through water.

[k] Total Cu input (water + aquafeeds and chemicals) minus Cu output (water + shrimp biomass).

(Burford et al., 2003; Jackson et al., 2003; Figueiredo et al., 2005).

Aquafeeds are by far the most significant source of Cu to the ponds, with high and variable concentrations, followed by lime and fertilizers (Table 4), which present similar and lower concentrations since Cu occurs in these substances as impurities. Total Cu load from aquafeeds and other products added to ponds contribute with 194.5 g ha^{-1} cycle^{-1}. Concentrations of Cu in shrimp biomass are in the same range of concentrations reported by other studies of *P.vannamei* (Páez-Ozuna et al., 2003). These concentrations are far below the maximum permissible concentrations for Cu in seafood for human consumption. Harvested shrimp biomass accounts for less than 10% of the Cu load added as aquafeeds and this excess Cu is the major responsible for the net Cu export estimated. Since the sum of Cu export through waters and Cu export through biomass does not account for the total Cu added as chemicals and aquafeed, part of the Cu input is probably retained in sediments. In this farm, Santos (2005) and Lacerda and Santos (2005) measured a slight increase in Cu concentrations in bottom sediments of ponds in the studied farm from 9.6 ± 4.7 μg g^{-1} at the 70th day of the growth cycle to 10.7 ± 4.6 at the 100th day to 15.2 ± 2.3 μg g^{-1} at the 135th day of the growth cycle, which could explain this imbalance by Cu sedimentation and accumulation in bottom sediments, which may eventually cause toxicity problem to shrimps after a certain number of cycles.

Assuming 2.3 production cycles per year typical of this farm and of others in NE Brazilian, Cu emission factors would reach 386.4 gCu ha^{-1} year^{-1}. Compared to other anthropogenic Cu sources to the Jaguaribe River estuary compiled by Lacerda et al. (2005) (Table 5), where urbanization is very low and industrialization non-existent, Cu emission factors from shrimp farming per unit of area per year is the highest among the specific emission factors for the other different activities under the present conditions of the Jaguaribe Basin. As expected, however, total emissions from shrimp farming compared to the other sources are less significant due to the small area occupied by shrimp farms (1.260 ha) relative to agriculture and urban areas.

We measure high Cu concentrations (up to 542 μg g^{-1}) in suspended particles in a mangrove creek about 600 m downstream of the effluent releasing point of the studied farm, resulting in a particulate Cu concentration of 34 μg L^{-1}, a 10-fold increase relative to measured particulate Cu in mangrove creek waters upstream from the farm intake (46 μg g^{-1} and 3.7 μg L^{-1}, respectively). Similarly, creek bottom

Table 5
Comparison of average Cu emission factors (g ha^{-1} yr^{-1}) and total annual emissions (t yr^{-1}) from different anthropogenic activities and processes (from Lacerda et al., 2005,) and shrimp farming at the Jaguaribe River estuary, NE Brazil

Activity	Cu emission factor at the Jaguaribe Basin	Cu annual emission to the Jaguaribe Basin
Agriculture	45.5	7.89
Wastewater disposal	2.5	0.43
Urban runoff	0.2	0.02
Solid wastes disposal	3.2	0.55
Husbandry	1.5	0.25
Shrimp farming	386.4	0.49

sediments presented mean Cu concentrations of 10.12 ± 0.8 $\mu g\, g^{-1}$ downstream the releasing point compared to 1.4 ± 0.5 $\mu g\, g^{-1}$, upstream the farm intake. However, average dissolved Cu in this sampling station (6.7 ± 0.3 $\mu g\, L^{-1}$) was not significantly different from upstream waters (6.6 ± 0.3 $\mu g\, L^{-1}$). This suggests a transport of particulate Cu contained in shrimp farm effluents to adjacent mangrove creeks.

In a study using mangrove oysters as metal monitors at the Curimataú River in Rio Grande do Norte, also in NE Brazil, Silva et al. (2003) found increasing Cu concentrations and availability in animals collected downstream the effluent releasing point of a larger shrimp farm. These authors suggested pond sediment remobilization and added Cu in aquafeeds as the source of the anomalous Cu concentrations found. Chou et al. (2002) also reported elevated concentrations of Cu in sediments under salmon cages in New Brunswick aquaculture and in lobsters collected in the same area. These results are in agreement with a net export of particulate Cu associated with intensive shrimp farm effluents suggested by our results.

The results presented here, although very preliminary, show that intensive shrimp farming presents the largest emission factors for Cu per unit of area in the region studied but contributes with relatively small discharges to the estuary when compared to other sources. However, since Cu emission from this source is directly disposed into estuarine waters and shrimp farming area is growing about 10% per year its impact on coastal ecosystem metabolism may become more significant than from other sources, as shown for nitrogen and phosphorus in other segments of the northeastern Brazilian coastline.

Acknowledgements

This study was supported by CNPq-Millenium Institute Program (Proc. No. 420.050/2005-1), FAPERJ through its PRONEX/FAPERJ Program project no. E26-171.175/2003 and FINEP/RECARCINE Initiative. We thank in particular Dr. S. Mounier and the Université de Toulon et du Var for the Cu analysis in water.

References

Bainy, A.C.D., 2000. Biochemical responses in penaeids caused by contaminants. Aquaculture 191, 163–168.

Boyd, C.E., Massaut, L., 1999. Risks associated with the use of chemicals in pond aquaculture. Aquaculture Engineering 20, 113–132.

Burford, M.A., Costanzo, S.D., Dennison, W.C., Jackson, C.J., Jone, A.B., McKinnon, A.D., Preston, N.P., Trott, L.A., 2003. A synthesis of dominant ecological processes in intensive shrimp ponds and adjacent coastal environments in NE Australia. Marine Pollution Bulletin 46, 1456–1469.

Chen, J., Lin, C., 2001. Toxicity of copper sulfate for survival, growth, molting and feeding of juveniles of the tiger shrimp Penaeus monodon. Aquaculture 192, 55–65.

Chou, C.L., Haya, K., Paon, L.A., Burridge, L., Moffatt, J.D., 2002. Aquaculture-related trace metals in sediments and lobsters and relevance to environmental monitoring program ratings for near-filed effects. Marine Pollution Bulletin 44, 1259–1268.

EEA (1999). Nutrients in European Ecosystems. Environmental Assessment Report No. 4, European Environmental Agency, Office for Official Publications of the European Communities, Luxemburg, 126 p.

EPA, 2002. National Recommended Water Quality Criteria. Environmental Protection Agency. Office of Water. EPA-822-R-02-047.

Figueiredo, M.C.B., Araújo, L.F.P., Gomes, R.B., Rosa, M.F., Paulino, W.D., Morais, L.F.S., 2005. Impactos ambientais do lançamento de efluentes da carcinicultura em águas interiores. Engenharia Sanitária e Ambiental 10, 167–174.

Hutton, M., Symon, C., 1986. The quantities of cadmium, lead, mercury and arsenic entering the UK environment from human activities. Science of the Total Environment 57, 129–150.

Jackson, C., Preston, N., Thompson, P.T., Burford, M.A., 2003. Nitrogen budget and effluent nitrogen components at an intensive shrimp far. Aquaculture 218, 397–411.

Lacerda, L.D., Santos, J.A. 2005. Distribution of Cu and Zn in farmed shrimp Litopennaeus vannamei from NE Brazil. In: Proceedings of the XIII International Conference on Heavy Metals in the Environment, Rio de Janeiro, CETEM, pp. 351–354.

Lacerda, L.D., Marins, R.V., Vaisman, A.G., Maia, S.R.R., Aguiar, J.E., Dias, F.J.S. 2004. Contaminação por metais pesados nas bacias inferiores dos Rios Curimataú e Açu (RN) e Rio Jaguaribe (CE). Sociedade Internacional par Ecossistemas de manguezal do Brasil; Instituto de Ciências do Mar, Associação Brasileira de Criadores de Camarão, Fortaleza, 63 p.

Lacerda, L.D., Marins, R.V., Dias, F.J.S., Aguiar, J.E., Vaisman, A.G., 2005. Heavy metals emissions and distribution along the Jaguaribe River lower basin, Northeastern, Brazil. In: Proceedings of the International Conference on Heavy metals in the Environment, Rio de Janeiro, CETEM, Rio de Janeiro, CD-Rom, 4 p.

Lacerda, L.D., Vaisman, A.G., Parente, L.P., Cunha, E., Silva, C.A.R., 2006. Relative importance of nitrogen and phosphorus emissions from shrimp farming and other anthropogenic sources for six estuaries along the NE Brazilian coast. Aquaculture 253, 433–446.

Lee, M., Shiau, S., 2002. Dietary copper requirement of juvenile grass shrimp Penaeus monodon and effects on non-specific immune response. Fish and Shellfish Immunology 13, 259–270.

Madrid, R.M., 2004. Influência do meio ambiente em áreas de risco na qualidade bacteriológica do camarão cultivado no Estado do Ceará. LABOMAR/UFC, Fortaleza, 233 p.

Molisani, M.M., Marins, R.V., Lacerda, L.D., 2004. Environmental changes in Sepetiba Bay, Brazil. Regional Environmental Change 4, 17–27.

Nriagu, J.O., Pacyna, J.M., 1988. Quantitative assessment of worldwide contamination of air, water and soils by trace metals. Nature 333, 134–139.

Páez-Ozuna, F., Garcia, A., Flores-Verdugo, F., Lyle-Fritch, L.P., Alonso-Rodrígues, R., Roque, A., Ruiz-Fernández, A.C., 2003. Shrimp aquaculture and the environment in the Gulf of California ecoregion. Marine Pollution Bulletin 46, 806–815.

Santos, J.A. 2005. Distribuição de Cu e Zn em fazendas de camarões cultivados no litoral leste do Estado do Ceará. M.Sc. Dissertation, Universidade Federal do Ceará, Fortaleza, 61 p.

Silva, C.A.R., Rainbow, P.S., Smith, B.D., 2003. Biomonitoring of trace metal contamination in mangrove-lined Brazilian coastal systems using oyster Crassostrea rhizophorae: comparative study of regions affected by oil, salt pond and shrimp farming activities. Hydrobiologia 501, 199–206.

Tacon, A.G.J., Forster, I.P., 2003. Aquafeeds and the environment: policy implications. Aquaculture 226, 181–189.

doi:10.1016/j.marpolbul.2006.09.012