



## Spatial and temporal variability of surface water pollution in the Mekong Delta, Vietnam



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### HIGHLIGHTS

- Usage of water in lower order canals of the Mekong Delta may lead to health concerns.
- Seasonality does not have major effects on water quality in lower order canals.
- A principal component analysis was used to identify contamination sources.
- Water quality was spatially visualized to identify hot-spot areas of pollution.

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### ABSTRACT

Surface water pollution in the Vietnamese Mekong Delta (MD) could threaten human, animal and ecosystem health given the fact that this water source is intensively used for drinking, irrigation and domestic services. We therefore determined the levels of pollution by organic pollutants, salts, metals and microbial indicators by (bi)monthly monitoring of canals between November 2011 and July 2012 at 32 sampling locations, representing fresh and saline/brackish environments. The results were compared with national water quality guidelines, between the studied regions and with water quality data from main waterways. Key factors explaining the observed levels of pollution in surface water were identified through principal component analysis (PCA). Temporal variations due to tidal regime and seasonality were also assessed. Based on regression models, the spatial variability of five water quality parameters was visualized using GIS based maps. Results indicate that pH (max. 8.6), turbidity (max. 461 FTU), maximum concentrations of ammonium ( $14.7 \text{ mg L}^{-1}$ ), arsenic ( $44.1 \mu\text{g L}^{-1}$ ), barium ( $157.5 \mu\text{g L}^{-1}$ ), chromium ( $84.7 \mu\text{g L}^{-1}$ ), mercury ( $45.5 \mu\text{g L}^{-1}$ ), manganese ( $1659.7 \mu\text{g L}^{-1}$ ), aluminum ( $14.5 \text{ mg L}^{-1}$ ), iron ( $17.0 \text{ mg L}^{-1}$ ) and the number of *Escherichia coli* ( $87,000 \text{ CFU } 100 \text{ mL}^{-1}$ ) and total coliforms ( $2,500,000 \text{ CFU } 100 \text{ mL}^{-1}$ ) in canals exceed the thresholds set by Vietnamese quality guidelines for drinking and domestic purposes. The PCA showed that i) urbanization; ii) metal leaching from soils; iii) aquaculture; and iv) tidal regime explain 85% of the variance of surface water quality attributes. Significant differences in water quality were found due to daily tidal regime and as a result of seasonality. Surface water quality maps for dissolved oxygen, ammonium, ortho-phosphate, manganese and total coliforms were developed to highlight hot-spot areas of pollution. The results of this study can assist policy makers in developing water management strategies and drinking water companies in selecting optimum water extraction locations.

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### 1. Introduction

In the Mekong Delta (MD), Vietnam and in other coastal regions of Southeast Asia, people rely on surface water not only for the irrigation of crops, aquaculture and the transportation of goods, but also for daily domestic uses including for drinking. Poor water quality and inadequate pre-treatment of surface water before use can lead to serious health risks and may be a contributing factor to the high mortality

rate of 8.5% of all deaths due to diarrhea in Southeast Asia (WHO, 2013). It is widely known that the quality of surface water in the region is threatened by a variety of pollutants from both natural and anthropogenic sources. The surface water quality in the MD is therefore regularly monitored not only by the provincial authorities (DONRE) and by the Mekong River Commission (MRC), but also by a number of time-bound projects, covering diverse pollutants (Sebesvari et al., 2012). The results of these studies show for example that pesticide residues in the aquatic environment can lead to a chronic exposure of humans and aquatic organisms (Toan et al., 2013). Due to the low topographical elevation of the MD, saline water intrusion is another water quality

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concern especially affecting rice production in coastal areas (Kotera et al., 2008). An assessment of microbial indicators of fecal pollution revealed high loads of *Escherichia coli* ( $10^2$ – $10^7$  CFU 100 mL<sup>-1</sup>) and total coliforms ( $10^3$ – $10^7$  CFU 100 mL<sup>-1</sup>) in many surface waters (Isobe et al., 2004). However, the concentrations of various heavy metals, including cadmium (Cd), copper (Cu), nickel (Ni) and lead (Pb), investigated in main waterways and coastal zones, were low compared to other catchment areas in the world (Cenci and Martin, 2004). The MRC also investigated water quality of the Mekong River in Laos, Thailand, Cambodia and Vietnam, and concluded that for most observation points, water quality was moderate to good with respect to nutrients and metals. However, salinity and especially acidity levels were found to be problematic within the delta (MRC, 2008).

In the MD, most investigations on surface water quality focus on acid sulfate soils (ASS), covering 40% of the total agricultural surface area (Guong and Hoa, 2012). The strong acidity in these soils increases the mobility of toxic elements, potentially affecting crop production, aquatic organisms and drinking water sources (Ljung et al., 2009). In the Plain of Reeds of the MD, pH values of 3.5 were associated with elevated concentrations of aluminum (Al) and iron (Fe) in the early wet season (Tin and Wilander, 1995; Husson et al., 2000). The observed Al concentrations of > 100 mg L<sup>-1</sup> exceeded the toxicity levels for fish and plant roots (Minh et al., 1997). Besides Al and Fe, other metals like Cd, Cu, Ni, Mn and Zn are present in higher concentrations in surface water than in areas with alluvial soils (Hoa et al., 2007).

Another important source of water contamination is aquaculture, leading to high levels of (bio)chemical oxygen demand (COD, BOD) and nutrients in water as a result of the applied fish food (Anh et al., 2010). Shrimp farming is a main activity in the coastal areas (e.g. in Soc Trang and Ca Mau provinces) leading to low concentrations of dissolved oxygen, while suspended solid concentrations are consistently high (Johnston et al., 2002). Furthermore, the effects of urbanization on surface water contamination are well recognized. Two independent studies in Ohio, USA showed clear correlations between electrical conductivity and concentrations of nutrients with urban land-uses (Wang and Yin, 1997; Tong and Chen, 2002). Similar findings were reported from urbanized areas in China (Wang et al., 2007), and a study conducted in Shanghai revealed that 94% of the variability in water quality was explained by industrial/domestic urban land uses (Ren et al., 2003). There are no comparable studies in the MD except for one report by Quyên et al. (1995) who concluded that both urbanization and industrialization are becoming serious threats to water quality.

Besides these anthropogenic and soil type-related sources of pollutants, climatic and seasonal effects are also found to influence water quality. Thus in the lower Mekong River, hydrological and climatological factors (precipitation, flow discharge, mean water level and air temperature) were strongly correlated with COD and dissolved oxygen concentrations in surface water (Prathumratana et al., 2008). Studies in Florida (USA), Spain and northern China revealed seasonal differences in water quality parameters (Ouyang et al., 2006; Vega et al., 1998; Chen et al., 2005). Similar studies in the MD are limited to a study by Stärz (2012) who investigated surface water quality in two districts of Can Tho province.

While many water quality studies have been conducted in the MD, most focused on either point sources or soil type effects or investigated the surface water quality in main waterways. The lower order canals are generally not included in monitoring programs. However, the total length of small man-made canals in the MD is more than 50,000 km (Truong, 2006), which is a factor of 10 higher than the entire length of the Mekong River. Both their hydrological regimes and their use by local population differ from the main waterways with a much more intensive use for various domestic purposes. It cannot a priori be assumed that the quality of these secondary canals is similar to that of the main waterways. It is therefore important to assess the water quality and its spatio-temporal variability in these lower order canals and to determine the potentially health-related risks associated with their use. To provide

insight into the water quality status and the main sources of pollution in lower order canals, this study addressed the following objectives: 1) analyze the water quality in lower order canals in representative areas and compare the results with Vietnamese guidelines for drinking and domestic use; 2) compare water quality in lower order canals between inland and coastal regions and water quality attributes from main waterways; 3) identify the factors which explain the spatial variability in surface water quality in lower order canals; 4) assess the effects of tidal regime and seasonality on water quality; and 5) spatially visualize water quality of these waterways to identify hot-spot areas of pollution.

## 2. Materials and methods

### 2.1. Study area

The MD is located in the south of Vietnam. Measurement locations in the MD were selected in three provinces: Can Tho, Hau Giang, and Soc Trang provinces (Fig. 1, presented as KML file in the supplementary data).

The Mekong River originates in the Tibetan Plateau and flows via China, Myanmar, Lao PDR and Thailand to Cambodia where it enters the Tonle Sap Lake. At this location, the Mekong River splits in nine branches (Cuu Long – or nine dragons in Vietnam) and flows through the MD in an easterly direction to the South China Sea. The climate in this tropical region is influenced by the southwestern monsoon (MRC, 2005). The wet season is generally between May and October with a mean annual rainfall of 1660 mm (23 years of measurements – Delta Alliance, 2011). During the wet season, 35%–50% of the total surface area of the MD is flooded (MRC, 2005). Sea-water intrusion dominates the hydrology along coastal areas with water level fluctuations >3 m per day due to tidal regime. Further inland in the MD, the diurnal tidal movement results in water level fluctuations of 1.0 m to 1.5 m between low and high tides (DONRE, 2011). The MD is well-known for its large density of artificial canals which are connected to the Mekong distributaries. These canals are of three different orders: the primary canals are used for irrigation and water discharge from agricultural fields. They mostly have very low flow velocities roughly between 0 and 1 m<sup>3</sup>/s and are dry during the dry season. The inlets and outlets of water in these waterways are often controlled by means of small gates. Secondary canals collect water from surrounding fields and primary canals and discharge into third order waterways (main canals, rivers). Secondary canals have a water flow of around 1–15 m<sup>3</sup>/s although in coastal regions the water flow is significantly higher (up to 30 m<sup>3</sup>/s) due to a strong influence from the tidal regime. Water flow in main rivers ranges between 400 and 6000 m<sup>3</sup>/s with the highest flow in the wet season (SIWRR, 2013). Land-use is dominated by intensive agriculture while natural vegetation such as forests occupies less than 10% of the area (MRC, 2005). The dominant land-use system is irrigated rice, representing nearly 50% of the agricultural production. Other agricultural activities include fruit orchards, aquaculture, shrimp farming, livestock rearing and the cultivation of upland crops (maize, sweet potatoes, sugar cane, vegetables) (GSO, 2010). Various types and mixtures of fertilizers were used in 2011–2012 in the MD in order to maintain and increase agricultural production particularly for rice cultivation, fruit orchards and other (upland) crops and include: i) different mixtures of N–P<sub>2</sub>O<sub>5</sub>–K<sub>2</sub>O; ii) urea (46% N); iii) DAP (di-ammonium phosphate; 16–48–0); iv) Lân Super (Ca<sub>3</sub>(H<sub>2</sub>PO<sub>4</sub>)<sub>2</sub>; 0–20–0); and v) Kali clorua (0–0–60). Farmers generally mix two or three of these fertilizers at application time. However, the type and location of agricultural activities are also strongly defined by soil types. Alluvial soils are mainly located near rivers and support diverse field crops; acid sulfate soils are mainly used for rice production; saline soils in coastal areas are mainly used for shrimp farming while degraded soils and sandy ridge soils along the eastern coastline are used mainly for upland crops and fruit orchards (Guong and Hoa, 2012). Main soil characteristics of the MD are mentioned in Supplementary material S1.1. Industrial activities

have developed rapidly in the region (Nghia, 2001). The total population of the MD was 17.3 million in 2011 (GSO, 2011). Inhabitants in rural areas settle mainly along primary and secondary canals while larger urban settlements are mostly located along the main waterways.

## 2.2. Sampling locations

Locations for surface water samplings were selected to obtain representative sites for the typical land uses (or in many cases land use mixtures) and soil types of the MD. These were identified using digital maps like satellite images and interviews with local authorities. Sites were subsequently validated in situ by investigating the actual land use and detecting potential disturbing factors (e.g. presence of fish farms in orchard dominated area). Sites were located on alluvial-, on slight to moderate acid sulfate- and on saline soils. A total of 32 sampling locations were divided into four areas: i) 18 locations were selected in the Can Tho province, representative for rice fields, fruit orchards, urbanized/industrial agglomerations, fresh water aquaculture and upland crops. Close to rivers, the soil type was alluvial while in the more inland locations soil types are slight acid sulfate soils; ii) nine locations were on moderate acid sulfate soils in Hoa An (Hau Giang province) representing combinations of rice fields and plots of upland crops such as sugarcane, maize and sweet potatoes; and iii) five locations were located on saline soils at Vinh Chau (Soc Trang province) representing a dense concentration of shrimp farms (Fig. 1). Each of the 27 locations in the Can Tho/Hau Giang provinces was sampled eight times between November 2011 and July 2012 on a monthly basis, whereas in the five locations in the coastal region of Soc Trang, sampling took place four times on a bi-monthly basis. The sampling period covered both the dry and the wet seasons. All samples were collected during outgoing tide defined by tide tables (DONRE, 2011). Only secondary canals were sampled. Primary canals were not considered due to the small water volume and the low flow velocities that make the water quality of these waterways extremely vulnerable to point source pollution such as the presence of ducks and local fish farming, which could disturb the potential relationship with land-use and/or soil type. Main canals and rivers, on the other hand, were mainly excluded as they contain water from a large variety of areas which complicates the isolation of the effects of land-use and/or soil types on water quality. However, five samples were collected in the Bassac River (a main branch of the Mekong River) in order to compare water quality with that of secondary canals.

## 2.3. Analytical procedures

Samples were analyzed for electrical conductivity (EC), total dissolved solids (TDS), pH, turbidity, dissolved oxygen (DO), chemical oxygen demand (COD), for salts (chloride ( $\text{Cl}^-$ ), sodium (Na)), for nutrients (ammonium ( $\text{NH}_4$ ), nitrate ( $\text{NO}_3$ ), nitrite ( $\text{NO}_2$ ), total-N and ortho-phosphate (o- $\text{PO}_4$ )), for metal(loid)s (arsenic (As), barium (Ba), cadmium (Cd), chromium (Cr), copper (Cu), mercury (Hg), manganese (Mn), nickel (Ni), zinc (Zn), aluminum (Al), iron (Fe) and magnesium (Mg)), and for microbial indicators (*E. coli*, other coliform bacteria and total coliforms). PE bottles (100 mL) were used to store water samples for COD, turbidity, TDS,  $\text{Cl}^-$  and nutrient analysis. For metal(loid) analysis PE bottles (50 mL) were filled with water samples and acidified with 1% nitric acid (65%, Merck Millipore, Billerica, MA, USA). Sterilized 100 mL glass bottles were used to store water for microbial analysis. Sampling was performed from boats or bridges in order to collect water from the center of the canals. Collection of water samples close to canal banks was always avoided since this water was often stagnant and could be of a different quality compared to the middle of the canals (i.e. washing of people close to canal banks). Sampling bottles were held 10–30 cm below the surface to prevent intrusion of floating debris and the openings of the sampling bottles were held in the opposite direction to that of the water flow. Bottles were closed under water

in order to prevent air intrusion. Directly after sampling, the bottles were stored in ice until they reached the laboratory within 8 h after collection. The EC, DO and pH were measured in-situ using a WTW Multi 340i instrument (Weilheim, Germany). For nutrients,  $\text{Cl}^-$  and COD, all samples were stored at 5 °C, pre-treated by syringe filters (0.45  $\mu\text{m}$ , Minisart Sartorius, Goettingen, Germany) and analyzed within 24 h of collection. The COD,  $\text{Cl}^-$ ,  $\text{NH}_4$ ,  $\text{NO}_2$ , total-N and o- $\text{PO}_4$  concentrations were measured by using Spectroquant® cell tests (Merck Millipore, Billerica, MA, USA) by applying the following ranges: COD 10–150  $\text{mg L}^{-1}$ ;  $\text{Cl}^-$  2.5–250  $\text{mg L}^{-1}$ ;  $\text{NH}_4\text{-N}$  0.20–8.00  $\text{mg L}^{-1}$ ;  $\text{NO}_2\text{-N}$  0.002–1.00  $\text{mg L}^{-1}$ ; total N 0.5–15.0  $\text{mg L}^{-1}$ ; and  $\text{PO}_4\text{-P}$  0.05–5.00  $\text{mg L}^{-1}$ .  $\text{NO}_3\text{-N}$  was measured using Spectroquant® cell test range 0.5–18.0  $\text{mg L}^{-1}$  although for measurement locations in Soc Trang, seawater proof cell tests were used from Spectroquant® cell test range 0.2–17.0  $\text{mg L}^{-1}$  (Merck Millipore, Billerica, MA, USA). Unfiltered water was used for turbidity measurements by using a HACH turbidimeter (Loveland, CO, USA) and TDS and was measured by WTW Profile Cond 197i (Weilheim, Germany) in unfiltered water. Samples for microbial analysis were treated within 8 h (EPA, 2002) after sampling under sterile conditions by plating 1 mL of unfiltered sample water on 3M™ Petrifilm™ coliform count plates (3 M, St. Paul, MN, USA). All samples were diluted twice ( $10^{-1}$  and  $10^{-2}$ ) with the exception of the samples from urbanized and industrial areas which were diluted three times ( $10^{-3}$ ). *E. coli* and other coliform colonies were counted  $24 \pm 4$  h after incubation at 37 °C. Acidified samples for metal analysis were stored in a fridge at 5 °C and analyzed within six months by inductively coupled plasma atomic emission spectroscopy (Thermo iCAP 6000, Thermo Scientific, FL, USA).

## 2.4. Data analysis

All statistical analyses were performed using SPSS 20.0 and geographical analyses using ArcGIS 10.

### 2.4.1. Water quality assessment

Water quality parameters were compared with Vietnamese guidelines established for drinking and domestic uses (Ministry of Health, 2009). The percentages of samples exceeding guideline values were calculated for both the inland areas (Can Tho/Hau Giang provinces) and the coastal region (Soc Trang) to compare water quality between these regions. Moreover, surface water quality in secondary canals was compared with water quality measurements based on the results of five sampling events in main waterways near Can Tho City and regular monitoring data of the MRC and the Deutsches GeoForschungsZentrum (GFZ) (MRC, 2007, 2008; GFZ, 2012).

Spatial differences in water quality were assessed by a principal component analysis (PCA). For this analysis, the initial dataset of 32 sampling locations containing annual median concentrations/levels for all water quality parameters was reduced to fulfill the criteria for the test (Bartlett test of sphericity, Kaiser–Meyer–Olkin measure of sampling adequacy (MSA) and determinant). First, all sampling locations at the coastal region were removed due to different hydrological and land-use systems as a result of sea water intrusion. A separate PCA for this region was not performed due to low amount of sampling locations (5). Second, all general parameters,  $\text{Cl}^-$ , total-N, Mg, *E. coli* and other coliforms caused multicollinearity and were removed. Third, the MSA test was negatively affected by  $\text{NO}_3$ , As, Cu and Cd due to the low variations in concentrations between the sites and they were therefore excluded from the dataset as well. The reduced dataset (COD, Na,  $\text{NH}_4$ ,  $\text{NO}_2$ , o- $\text{PO}_4$ , Al, Ba, Cr, Fe, Hg, Mn, Ni, Zn, total coliforms) was further rotated by varimax with Kaiser normalization to express the loadings in explaining components.

### 2.4.2. Temporal variability

The dataset of the 32 sampling sites contains water quality measurements from the dry and wet seasons in 2011/2012 and was used to

assess seasonal differences in water quality at both inland and coastal regions. The water quality in the dry and wet seasons was statistically compared with the non-parametric Kruskal–Wallis test since the criteria of normal distribution was not met. The differences in water quality between seasons were visualized by box-and-whisker diagrams for ten representative water quality parameters.

The variability of water quality by the tidal regime was investigated by a measurement station located in a tributary of the Hau River near Can Tho City (GFZ, 2012). The distance of this station to the Hau River was less than a hundred meters. Water was measured every 15 min for water level and for EC, TDS, DO and pH levels. The water levels and EC values were plotted graphically from 9 July 2012 to 14 July 2012 to investigate daily fluctuations as a result of the tidal regime.

#### 2.4.3. Water quality maps

Surface water quality maps were developed by linear regression models with land-use and river distance as explaining variables. The water quality parameters DO,  $\text{NH}_4$ ,  $\text{o-PO}_4$ , Mn and total coliforms were selected for their strong relationship with either land-use and/or distance to rivers (see also Supplementary material S1.2) and represented different groups of water quality parameters as well. The land-use map (Huth et al., 2012) used for regression analysis only covered parts of the Can Tho and Hau Giang provinces and therefore only surface water quality maps of these regions are presented. Median yearly concentrations of twenty sampling locations in Can Tho and Hau Giang were used for regression since these fell within the extent of the land-use map. The concentrations were log-transformed to meet the criteria of the regression analysis (linearity, constant variances, normal distribution, outliers). Only the predicting variables (land-use and river distance) that were significantly correlated (Pearson correlation test) with the water quality parameters were used for the linear regression models. Spatial visualization was performed by dividing the entire land-use map of Can Tho/Hau Giang provinces from 2010 (accuracy of 93.7%; ultimate spatial resolution of 10 m (Huth et al., 2012)), in grids of 750–750 m (resulting in 4144 grid cells). For each grid cell, the percentage of land-use systems and distance to river was defined. The regression models were then used to calculate the concentrations of the selected substances for each grid cell based on this information. The predicted concentrations of each grid cell were interpolated with inverse distance weighting to generate smooth maps. The predicted water quality maps were validated by the data from three independent locations. Two measurement locations were purposely excluded for regression analysis to function as validation points. Another validation location was selected from a small scale study area where surface water quality was assessed in a commune close to Can Tho City (Stärz, 2012). The three selected validation locations were geographically spread to cover the entire study area. Validation was carried out by comparing the observed (measured from field data) concentrations with the regression modeled 95% interval confidence range concentrations at the three validation locations. If the observed concentrations from these independent measurement locations fell within the modeled confidence range, the regression model was validated.

### 3. Results and discussion

#### 3.1. Differences in water quality between sites and waterways

Table 1 shows all analyzed water quality parameters in secondary canals at inland sampling stations (Can Tho/Hau Giang provinces) and at a coastal region that is influenced by sea water intrusion (Soc Trang province). The median concentrations of five measurements in rivers as well as river water quality data from the Mekong River Commission (MRC, 2007, 2008) and GFZ (2012) are included to compare water quality between secondary canals and river water.

#### 3.1.1. Dissolved oxygen, COD and turbidity

Table 1 shows that extremely low DO concentrations were observed in waters of the inland regions compared to waters in the coastal areas and in rivers. Significantly higher COD concentrations were detected in lower order canals of the inland region compared to river water. In the waters of the coastal region, high Cl concentrations interfered with COD measurements, so data are not shown. Turbidity levels were highest in lower order canals of the coastal region but drinking and domestic water quality guidelines were exceeded at all investigated sites. High turbidity levels in the coastal region were probably caused by stronger flow velocities in coastal canals due to a strong influence of the tidal regime causing fluctuations in water levels of several meters per day. Peak levels of turbidity were also found in urbanized and industrial areas at inland regions most probably caused by untreated waste water effluents. The findings of lower DO and higher COD concentrations in secondary canals of inland regions compared to main rivers suggest that these smaller waterways are more polluted with organic matters. This could be explained by low flow velocities and volumes in combination with intensive use and discharge of waste (visually observed during field visits), leading to the accumulation of organic pollutants. Nevertheless, DO concentrations in secondary canals of the coastal region were higher than those of the inland regions which could be the result of continuous sea water intrusion. DO concentrations in seawater can vary between 3.0 and 9.7  $\text{mg L}^{-1}$  as shown in a study near Hong Kong (EPD, 2008). When surface water is used as drinking/domestic water source it is recommended to use river water instead of secondary canal water due to the accumulating organic pollutants in these waterways. Moreover, surface water needs to be treated intensively in all circumstances to remove organic pollutants and the high levels of turbidity.

#### 3.1.2. Salts

Elevated concentrations of Na and Cl (originating from sea water, sewage water and agricultural soils) increase the electrical conductivity of the water and reduce the suitability for human consumption and irrigation purposes. The highest concentrations of salts (Na and Cl) are found in the secondary canals of the coastal areas exceeding drinking water guidelines for almost all samples. In contrast, guideline values were not exceeded in secondary canals in inland regions and in river water. The constantly high Na and Cl concentrations in the coastal region do not only limit the use of surface water for drinking and domestic purposes but also severely impact rice production. During field visits, it was observed that rice fields in this region are left fallow as cultivation is hampered by saline water intrusion. This finding was also reported by Kotera et al. (2008), who detected salt concentrations of up to 35  $\text{g L}^{-1}$  in coastal regions of the MD with significant impacts on rice production. The significantly lower salt concentrations in the inland regions suggest that sea water intrusion does not reach the Can Tho/Hau Giang provinces which was also found by a study of White (2002). Nevertheless, salt concentrations in surface waters in secondary canals of the inland regions were higher compared to river water. Secondary canals in the Can Tho/Hau Giang regions receive water from surrounding areas (i.e. rice fields and direct effluents of point sources), locally raising water salinity. Moreover, the exchange rate of these waters is lower, leading to accumulations of salts. In general, surface water in coastal regions is too saline for human consumption and irrigation purposes. However, canal water in inland regions and main river water does not exceed the guidelines for Cl and Na.

#### 3.1.3. Nutrients

Emissions of (untreated) sewage water and run-off from fertilized agricultural soils are major sources of nutrients in surface water. In rural areas, mainly dominated by rice cultivation, the amount of fertilizer use has vastly increased in the last decades with average total fertilizer use ranging from 40  $\text{kg ha}^{-1}$  in 1976 to over 220  $\text{kg ha}^{-1}$  in the

**Table 1**  
Annual median concentrations/levels, range and guideline exceedance of the surface water quality in secondary canals for physico-chemical parameters, salts, nutrients, metals and microbial indicator bacteria at inland and coastal regions. The median concentrations/values of water quality in main waterways from own observations and other studies are presented to compare with water quality in secondary canals.

|  | VN guidelines <sup>a</sup> |          | Inland regions (Can Tho/Hau Giang) |        |        |           |                      |                    | Coastal region (Soc Trang) |        |        |        |                      |                    | River water           |                  |                  |
|--|----------------------------|----------|------------------------------------|--------|--------|-----------|----------------------|--------------------|----------------------------|--------|--------|--------|----------------------|--------------------|-----------------------|------------------|------------------|
|  | Drinking                   | Domestic | N                                  | Median | Min    | Max       | %Drink. <sup>b</sup> | %Dom. <sup>c</sup> | N                          | Median | Min    | Max    | %Drink. <sup>b</sup> | %Dom. <sup>c</sup> | Own data <sup>d</sup> | MRC <sup>e</sup> | GFZ <sup>f</sup> |
| <i>Phy. chem. parameters</i>               |                            |          |                                    |        |        |           |                      |                    |                            |        |        |        |                      |                    |                       |                  |                  |
| EC (dS m <sup>-1</sup> )                   | –                          | –        | 223                                | 1.8    | 0.9    | 8.2       | –                    | –                  | 25                         | 92.5   | 5.3    | 434.0  | –                    | –                  | 1.2                   | 0.2              | 0.10–0.15        |
| TDS (mg L <sup>-1</sup> )                  | 1000                       | –        | 218                                | 191    | 101    | 835       | 0                    | –                  | 14                         | 5098   | 115    | 74,600 | 77                   | –                  | 132                   | –                | –                |
| pH   | 6.5–8.5                    | 6.0–8.5  | 223                                | 6.8    | 6.2    | 7.4       | 11                   | 0                  | 25                         | 7.7    | 6.9    | 8.6    | 0                    | 0                  | 7.5                   | 7.2              | 7.4–7.7          |
| Turbidity (FTU)                            | 2                          | 5        | 223                                | 92     | 18     | 461       | 100                  | 100                | 25                         | 157    | 44     | 457    | 100                  | 100                | 96                    | –                | 10–250           |
| DO (mg L <sup>-1</sup> )                   | –                          | –        | 223                                | 1.7    | 0.0    | 5.0       | –                    | –                  | 25                         | 6.0    | 2.4    | 7.6    | –                    | –                  | 4.6                   | 6.7              | 2.0–5.0          |
| COD (mg L <sup>-1</sup> )                  | –                          | –        | 165                                | 22     | <10    | 88        | –                    | –                  | –                          | –      | –      | –      | –                    | 9                  | 4.8                   | –                | –                |
| <i>Salts</i>                               |                            |          |                                    |        |        |           |                      |                    |                            |        |        |        |                      |                    |                       |                  |                  |
| Cl (mg L <sup>-1</sup> )                   | 250                        | –        | 94                                 | 16     | 6      | 130       | 0                    | –                  | 15                         | 2757   | 110    | 18,070 | 64                   | –                  | 7                     | 9                | –                |
| Na (mg L <sup>-1</sup> )                   | 200                        | –        | 101                                | 1.5    | 0.4    | 7.3       | 0                    | –                  | 25                         | 204.8  | 11.3   | 761.9  | 100                  | –                  | 0.7                   | 2.8              | –                |
| <i>Nutrients</i>                           |                            |          |                                    |        |        |           |                      |                    |                            |        |        |        |                      |                    |                       |                  |                  |
| NH <sub>4</sub> (mg L <sup>-1</sup> )      | 3                          | 3        | 223                                | 0.8    | <0.2   | 14.7      | 12                   | 12                 | 25                         | 0.3    | <0.2   | 2.2    | 0                    | 0                  | 0.2                   | 0.16             | –                |
| NO <sub>3</sub> (mg L <sup>-1</sup> )      | 50                         | –        | 223                                | 0.6    | <0.5   | 2.9       | 0                    | –                  | 25                         | <0.5   | <0.5   | 0.5    | 0                    | –                  | 0.5                   | 0.30             | –                |
| NO <sub>2</sub> (mg L <sup>-1</sup> )      | 3                          | –        | 223                                | 0.050  | <0.002 | 0.290     | 0                    | –                  | 25                         | 0.010  | <0.002 | 0.210  | 0                    | –                  | 0.009                 | –                | –                |
| Total N (mg L <sup>-1</sup> )              | –                          | –        | 72                                 | 2.7    | <0.5   | 17.1      | –                    | –                  | –                          | –      | –      | –      | –                    | –                  | –                     | –                | –                |
| o-PO <sub>4</sub> (mg L <sup>-1</sup> )    | –                          | –        | 223                                | 0.20   | <0.05  | 3.90      | –                    | –                  | 25                         | 0.10   | <0.05  | 0.40   | –                    | –                  | 0.16                  | 0.10             | –                |
| <i>Metal(loid)s</i>                        |                            |          |                                    |        |        |           |                      |                    |                            |        |        |        |                      |                    |                       |                  |                  |
| As (µg L <sup>-1</sup> )                   | 10                         | 10       | 101                                | 2.4    | <2.0   | 44.1      | 11                   | 11                 | 25                         | 4.9    | <2.0   | 39.5   | 14                   | 14                 | 3.1                   | –                | –                |
| Ba (µg L <sup>-1</sup> )                   | 700                        | –        | 101                                | 42.2   | 8.1    | 157.5     | 0                    | –                  | 25                         | 40.3   | 17.6   | 82.9   | 0                    | –                  | 68.6                  | –                | –                |
| Cd (µg L <sup>-1</sup> )                   | 3                          | –        | 101                                | 0.2    | <0.1   | 1.7       | 0                    | –                  | 25                         | 0.2    | <0.1   | 0.6    | 0                    | –                  | 0.1                   | –                | –                |
| Cr (µg L <sup>-1</sup> )                   | 50                         | –        | 101                                | 4.8    | <0.4   | 84.7      | 1                    | –                  | 25                         | 8.2    | 1.9    | 21.7   | 0                    | –                  | 6.1                   | –                | –                |
| Cu (µg L <sup>-1</sup> )                   | 1000                       | –        | 101                                | 3.2    | <0.3   | 36.8      | 0                    | –                  | 25                         | 6.0    | 2.1    | 39.1   | 0                    | –                  | 3.5                   | –                | –                |
| Hg (µg L <sup>-1</sup> )                   | 1                          | –        | 101                                | 1.6    | <1.2   | 45.5      | 67                   | –                  | 25                         | 1.8    | <1.2   | 13.7   | 72                   | –                  | 1.6                   | –                | –                |
| Mn (µg L <sup>-1</sup> )                   | 300                        | –        | 101                                | 281.6  | 59.3   | 919.4     | 49                   | –                  | 25                         | 389.3  | 26.0   | 1659.7 | 72                   | –                  | 73.8                  | –                | –                |
| Ni (µg L <sup>-1</sup> )                   | 20                         | –        | 101                                | 2.9    | 0.5    | 13.3      | 0                    | –                  | 25                         | 3.6    | <0.4   | 14.9   | 0                    | –                  | 3.1                   | –                | –                |
| Zn (µg L <sup>-1</sup> )                   | 3000                       | –        | 101                                | 10.1   | <0.1   | 108.0     | 0                    | –                  | 25                         | 17.0   | 2.5    | 44.9   | 0                    | –                  | 10.2                  | –                | –                |
| Al (mg L <sup>-1</sup> )                   | 0.2                        | –        | 101                                | 1.9    | 0.2    | 9.3       | 99                   | –                  | 25                         | 3.7    | 0.1    | 14.5   | 96                   | –                  | 3.2                   | –                | –                |
| Fe (mg L <sup>-1</sup> )                   | 0.3                        | 0.5      | 101                                | 2.7    | 0.6    | 15.7      | 100                  | 100                | 25                         | 5.1    | <0.3   | 17.0   | 96                   | 96                 | 3.6                   | –                | –                |
| Mg (mg L <sup>-1</sup> )                   | –                          | –        | 101                                | 5.6    | 2.3    | 11.2      | –                    | –                  | 25                         | 158.6  | 153.4  | 417.3  | –                    | –                  | 3.2                   | 5                | –                |
| <i>Microbial indicators</i>                |                            |          |                                    |        |        |           |                      |                    |                            |        |        |        |                      |                    |                       |                  |                  |
| <i>E. coli</i> (CFU 100 mL <sup>-1</sup> ) | 0                          | 0        | 223                                | 3484   | 180    | 87,272    | 100                  | 100                | 25                         | 2713   | ND     | 30,000 | 80                   | 80                 | 1432                  | –                | –                |
| Other coli. (CFU 100 mL <sup>-1</sup> )    | 0                          | 50       | 223                                | 12,851 | 2072   | 2,481,818 | 100                  | 100                | 25                         | 5450   | 90     | 34,546 | 100                  | 100                | 5686                  | –                | –                |
| Total coli. (CFU 100 mL <sup>-1</sup> )    | 0                          | 50       | 223                                | 16,335 | 2252   | 2,569,090 | 100                  | 100                | 25                         | 8163   | 90     | 64,546 | 100                  | 100                | 7118                  | –                | –                |

N: number of samples; ND: not detected; –: no guideline value set.

<sup>a</sup> Vietnamese water quality standards (Ministry of Health, 2009).

<sup>b</sup> Percentage of water samples exceeding the Vietnamese drinking water quality guidelines.

<sup>c</sup> Percentage of water samples exceeding the Vietnamese domestic water quality guidelines.

<sup>d</sup> Data collected in the Hau River near Can Tho City (n = 3 for metals and n = 5 for other parameters).

<sup>e</sup> Water quality data extracted from research by the Mekong River Commission (MRC, 2007; MRC, 2008).

<sup>f</sup> Data extracted from a continuous water quality measurement station in Hau River near Can Tho City between October 2011 and October 2012 (GFZ, 2012).

period 1995–2003 (Berg, 2002; Dung, 2007; Lang et al., 2008). More recently, own interviews conducted with 117 rice farmers in the MD revealed that 105.5 kg ha<sup>-1</sup> of nitrogen, 73.1 kg ha<sup>-1</sup> of P<sub>2</sub>O<sub>5</sub> and 48.0 kg ha<sup>-1</sup> of K<sub>2</sub>O were used in the wet season of 2011 while fertilizer use in the dry season was lower (81.4 kg ha<sup>-1</sup> nitrogen; 27.7 kg ha<sup>-1</sup> P<sub>2</sub>O<sub>5</sub>; 44.4 kg ha<sup>-1</sup> K<sub>2</sub>O). The large quantities of fertilizers applied by farmers could partially run off from agricultural fields into the secondary canals. Moreover, primary agricultural field canals do often discharge surplus of water directly to secondary canals. This could explain the observed elevated concentrations of NH<sub>4</sub>, total-N and o-PO<sub>4</sub> in secondary canals that were present at almost all locations in the MD. Furthermore, potassium (not investigated in this study) is present in elevated concentrations in lower order canals within the range 1.8–2.1 mg L<sup>-1</sup>, as shown by a study of Hoa et al. (2006) in Can Tho and Dong Thap provinces of the MD. However, the exact relationship between fertilizer application on agricultural fields and water quality should be further assessed. In addition, (in)direct sewage effluents from villages and cities may be another cause for elevated concentrations of these nutrients in water. Nutrient concentrations in water are also strongly dependent on several conditions (i.e. temperature, DO concentrations, sunlight penetration) of the receiving water body.

Although relatively high NH<sub>4</sub>, o-PO<sub>4</sub> and total-N concentrations were detected in the secondary canals of the inland region this was not observed for NO<sub>2</sub> and NO<sub>3</sub>. Instead, the concentrations of these nutrients were low when compared to drinking water guidelines. The low NO<sub>2</sub> and NO<sub>3</sub> concentrations could be caused by the generally low redox potential or DO content, limiting nitrification processes. While, some oxygen was found in the top-layer of the surface water, the concentrations declined rapidly with increasing depths (Johnston et al., 2002). Moreover, available nitrate would be rapidly transformed to N<sub>2</sub>O or N<sub>2</sub> due to conditions favoring denitrification. In general, the nutrient concentrations in the coastal region were lower compared to the inland regions. Sea water usually contains lower concentrations of nutrients than fresh water bodies which is confirmed by a variety of studies on coastal water quality such as in Hong Kong and Europe (EPD, 2008; EEA, 2011). Moreover, pollution from point sources is expected to be diluted in the coastal region due to the strong flow velocities in these canals. The lowest NH<sub>4</sub> concentrations were found in main rivers compared to secondary canals. In addition to dilution effect, this could be explained by the higher concentrations of dissolved oxygen in rivers which enhances ammonification and nitrification processes in those main waterways.

Although water quality guidelines for nutrients were exceeded for NH<sub>4</sub>, observed nutrient concentrations in the MD generally pose little risks associated with drinking and domestic services. High concentrations of NO<sub>2</sub> and NO<sub>3</sub> in drinking water for example, may cause methemoglobinemia (Camargo and Alonso, 2006). However, in the MD concentrations of these nutrients are low indicating that those health risks are unlikely to occur.

### 3.1.4. Metal(loid)s

The presence of metals in surface water can be explained by both natural (i.e. metallic agents that are made available and mobile via reduced conditions) and anthropogenic (i.e. emissions of industrial and/or urban waste water) sources. In the MD, metal(loid) concentrations in secondary canals exceeded drinking water guidelines for As, Cr, Hg, Mn, Al and Fe. Most metal concentrations in coastal regions were higher compared to inland regions. The concentrations of most metal(loid)s in main waterways were similar to those in inland lower order canals except for Ba, Mg and Mn.

The generally low As concentrations in surface water is likely caused by the presence of Fe and Al which reduces the release of As to surface water (Guong and Hoa, 2012). However, the reported peak concentrations with similar concentration levels between 35 and 45 µg L<sup>-1</sup> were most probably caused by drainage and excavation of canals which lead to oxidation of As-containing sulfide compounds that leach out to the surface water (Guong and Hoa, 2012). Drainage and excavation of canals

were observed in many sampled locations during the dry season, due to lower water levels and flow velocities compared to the wet season. This is in line with the observed peaks of As which were detected only during the dry season for short periods of time (<2 months). This observation is relevant since local populations usually collect surface water for drinking during the dry season when other preferred sources like rainwater are not available. The highest Ba concentrations in the MD were found in river water. This could be explained by barite mining activities in riparian countries which result in Ba rich effluents to the Mekong River (Fong-sam et al., 2012). Nevertheless, Ba concentrations did not exceed drinking water guidelines. In contrast, Al and Fe concentrations exceeded drinking water quality guidelines for almost all samples. The presence of these metals is well known in the surface waters of the MD in areas where acid sulfate soils dominate. In these soils, the oxidation of pyrite causes a leaching of these substances to surface waters (Tin and Wilander, 1995). However, Al and Fe concentrations in our study are lower when compared with other studies in the region which showed maximum concentrations of Fe and Al of 182 mg L<sup>-1</sup> and 104 mg L<sup>-1</sup>, respectively (Husson et al., 2000; Hoa et al., 2007). Moreover, pH levels in our study were generally observed in the neutral range (6.0–8.0) while in typical ASS, pH levels drop to <3.5 (Minh et al., 1997). Hg is another metal that exceeds drinking water guidelines at most locations. The presence of this metal is most probably caused by anthropogenic emissions from industrial and urbanized activities. In general, the highest observed metal concentrations were found in secondary canals of the coastal region which may be the result of significantly higher turbidity levels due to stronger flow velocities compared to inland canals. It is well known that metals are strongly bound to suspended solids. Therefore, water with higher turbidity could result in elevated amounts of total metals in comparison with areas that have lower turbidity levels. However, the elevated Mn and Mg concentrations could also be the result of sea water intrusion.

Surface water in the MD was found to exceed drinking water guidelines for a variety of metals especially at secondary canals in the coastal region. The consumption of surface water of secondary canals can therefore lead to severe health-related concerns. This finding is in contradiction with studies to heavy metal concentrations in main rivers of the MD, that concluded that water quality in main rivers with respect to metals was moderate to good and does not cause any level of concern with respect to human health (MRC, 2007). The finding of this study with respect to metal concentrations in secondary canal is relevant since many people in the MD rely on this water source for drinking and/or domestic purposes.

### 3.1.5. Microbial indicator bacteria

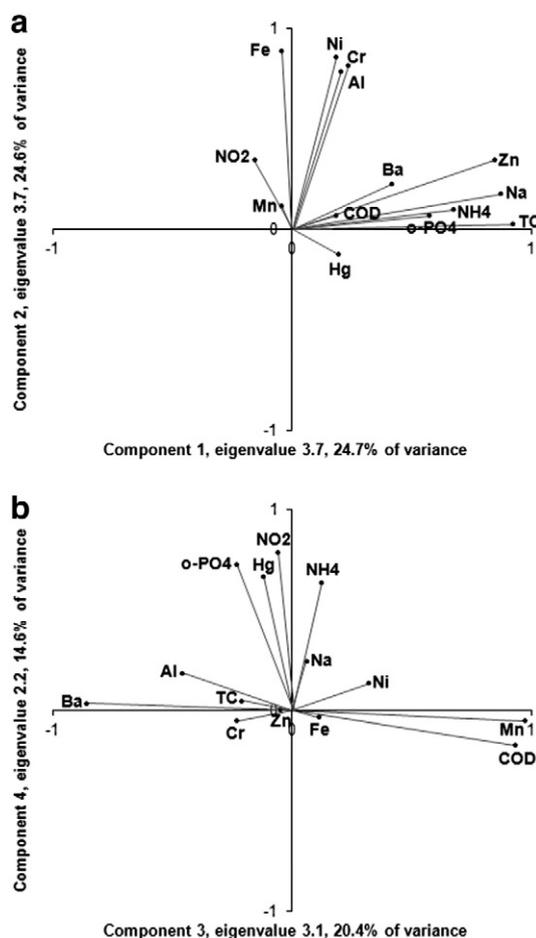
The number of *E. coli* and other coliform bacteria indicates fecal contamination of the water and are of critical concern with respect to human health. The cell counts of *E. coli* as well as other coliforms were high and exceeded thresholds for drinking water in both regions as well as in river water. This finding is similar to that reported by Isobe et al. (2004) who found *E. coli* cell counts between 10<sup>2</sup> and 10<sup>6</sup> CFU 100 mL<sup>-1</sup> and total coliforms in the range 10<sup>3</sup>–10<sup>7</sup> CFU 100 mL<sup>-1</sup> defined from 22 measurement locations spread over the MD. The high microbial pollution was likely caused by a variety of sources. Firstly, sewage water is rarely treated and is discharged directly to the surface water; a second source could be the presence of animal farms that usually release waste to the environment with no or only primary treatment and a third reason could be that ducks are often raised in canals especially after rice harvesting. A study of microbial pollution in Georgia, USA where sewage water treatments are more common, found *E. coli* concentrations usually in the range <10<sup>3</sup> CFU 100 mL<sup>-1</sup> (Fisher et al., 2000). These concentrations are considerably lower compared with the MD and could confirm the effects of lack of sewage water treatment.

The observed cell counts of microbial indicator bacteria in our study varied between the investigated regions. The highest pollution was observed in the inland region of Can Tho/Hau Giang while in river water pollution was lowest. In Soc Trang province, concentrations are 1.3–2.0 times lower compared with the inland region which may be the result of lower population densities, the scarcity of animal farms and strong dilution effects. However, salinity tolerance could also explain the lower observed concentrations of fecal contaminants. The average concentrations of microbial indicator bacteria in main waterways were considerably lower compared to surface waters in the secondary canals. This could be explained by a strong dilution of point source emissions by large water volumes and higher flow velocities.

Although, microbial indicators are widely detected in the MD, households usually treat surface water (e.g. boiling and/or chemically) prior to drinking which could decrease the actual health risks associated with consuming surface water. However, this is not the case for other domestic uses such as dish washing, washing vegetables and fruits prior to consumption which might put the population at risk.

### 3.2. Spatial variability of water quality

A principal component analysis was performed to investigate which were the main factors explaining the presence of organic pollution (COD), salts, nutrients, heavy metals and microbial pollution in surface water of secondary canals (Fig. 2). Four factors with eigenvalues >1 were extracted explaining ca. 85% of the total variance of surface water contamination for the selected parameters.



**Fig. 2.** Loadings of water quality parameters in four principal components (a: components 1 and 2; b: components 3 and 4) with eigenvalues >1. Note: rotation by varimax with Kaiser normalization is performed. The dataset contains a reduced amount of water quality parameters in order to meet the criteria of the analysis. TC: total coliforms.

The first component is mainly characterized by Zn, Na and total coliforms. Also NH<sub>4</sub> and o-PO<sub>4</sub> have high loadings compared to other water quality parameters. This component is interpreted as 'urbanization-related pollution'. Coliform, NH<sub>4</sub> and o-PO<sub>4</sub> concentrations were generally high at measurement locations influenced by villages, cities and industrial areas compared to agricultural rural areas which illustrate the impact of untreated sewage water inputs on surface waters. In addition, Zn had the highest concentrations near urbanized areas likely caused by the presence of metal roofs that leach out metals such as Zn during rainfall events. Wilbers et al. (2013) found Zn concentrations in harvested rainwater from metal sheet roofs with maximum concentrations of 2.21 mg L<sup>-1</sup> in the MD. It could explain the higher concentrations of Zn at urbanized locations given the high density of population in villages and cities compared to the rural areas. Na could be explained by emissions of industrial activities as is confirmed by the higher observed salt concentrations (Na: 7.3 mg L<sup>-1</sup>; Cl: 130 mg L<sup>-1</sup>) in surface water at a measurement location near an industrial area. The relation between urbanization and elevated concentrations of NH<sub>4</sub>, coliforms and metals is also reported by Ren et al. (2003) who found a strong positive correlation between urban land use and worsening water quality classifications in Shanghai. Furthermore, a study of the relationship between land-use and water quality in Miami, USA revealed a positive relationship between EC and the percentage of urban land-use (Wang et al., 2007).

The second component comprises Al, Fe, Cr and Ni and is interpreted as 'soil leaching' given the high loadings for the earth metals Al and Fe in the PCA. All the metals in this component were detected in all surface water samples, only the concentrations differed. The effects of metal leaching from soils were also observed by Hoa et al. (2007) who found relationships between the presence of metals in surface water (including Al, Fe and Ni) and different acid soil types in the MD. Although severe ASS were not found in our study, this could nevertheless explain the presence of these metals in surface water (see also Supplementary data S1.1).

The third component comprises COD, Mn and Ba. This pattern is most probably related to the effects of 'mixing with fresh water due to the tidal regime' in the secondary canals. Usually water from secondary canals is refreshed by river water as a result of the tidal movements. However, at locations further away from main rivers these tidal movements may not be sufficient or do not occur at all, leading to a lack of mixing which could result in an accumulation of pollutants such as COD and Mn. Two locations with distances to the Hau River of 0 and 10 km were used to investigate the impact of the tidal regime related to river distance. The water levels of the location close to the Hau River (distance 0 km) differed by 1.8 m between low and high tides while the location further away from the Mekong River (distance 10 km) only showed variations of 0.7 m (GFZ, 2012). This confirms the reduced impact of mixing with fresh water with increasing river distance. Moreover, the effects of differences in tidal regime between locations were also observed during field visits when it was visible that canals that lacked tidal movements were more heavily polluted by organic waste compared with canals closer to main rivers. Similar results are also found in the UK, where decreased flow velocities and less mixing of water were shown to lead to higher concentrations of organic pollutants and lower dissolved oxygen concentrations (Whitehead et al., 2009). Although an accumulation of Mn was observed in areas that lacked tidal movements, this pattern was not observed for other earth metals like Al, Cr and Ni. The negative high loading for Ba (-0.86) is in line with the observation that river water contains higher Ba concentrations compared with lower order canals (see also Supplementary data S1.3). This also confirms the influence of the tidal regime on water quality.

The fourth component comprises NH<sub>4</sub>, NO<sub>2</sub>, o-PO<sub>4</sub> and Hg and is interpreted as the influence of 'aquaculture' on surface water. This is supported by the fact that elevated concentrations of all the mentioned nutrients and Hg were observed at sites near fish farms. The presence of

Hg in surface water receiving effluents from fish farms is furthermore confirmed by Choi and Cech (1998) who found unexpectedly high concentrations of Hg in pelleted commercial fish feed. Moreover, a study in Canada detected higher concentrations of Hg in rockfish at locations close to salmon farms (DeBruyn et al., 2006).

### 3.3. Temporal fluctuations of water quality

#### 3.3.1. Tidal movements

Surface water in the MD is influenced by two diurnal tidal movements. This causes fluctuations in water level and impacts water quality due to variations in the dilution of (non)point sources of pollution. Daily variations in water level and quality (EC) due to the tidal regime are shown in Fig. 3 (data: GFZ, 2012).

The highest observed EC levels are visible during outgoing tide (decreasing water levels) which indicates the effects of accumulation of pollutants. The lowest EC levels are observed during incoming tide as a result of fresh river water that has not been severely contaminated yet. Similar results to that of EC are found for concentrations of TDS and DO. However, it was found that pH levels, water temperature and turbidity concentrations did not fluctuate as a result of tidal movements. Nevertheless, the variation of EC levels due to the tidal regime indicates that water quality parameters such as nutrients ( $\text{NH}_4$ ), salts and some metals may show similar patterns. This finding was confirmed by another study on water quality in the MD that found differences in nutrient concentrations between low and high tides (Stärz, 2012). On the other hand, the further inland locations most probably show lower differences in water quality between the tides since tidal fluctuations decrease with increasing river distance from the coastline. Nevertheless, in cases wherein surface water is used for drinking and domestic purposes, it is recommended to collect water during high tide since most pollutants are diluted, a practice generally respected by households in the region.

#### 3.3.2. Seasonality

The monsoonal climate of the MD generates dry and wet seasons. Variations in rainfall events and quantity between seasons affect dilution of pollutants. Fig. 4 shows the seasonal water quality for several representative parameters (pH, turbidity, COD/DO, Cl,  $\text{NO}_3$ , o- $\text{PO}_4$ , Fe, Mn, Zn and total coliforms) at the inland and coastal regions.

Fig. 4 shows that there are slightly but statistically significantly lower pH values in the wet season in both regions. This may be the result of higher run-off rates of (acid) soils in the (early) wet season compared with the dry season. Also the higher turbidity and Fe concentrations that were observed in the wet season may confirm this pattern.

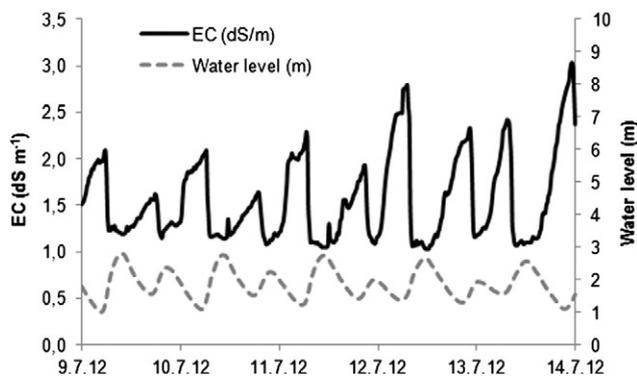


Fig. 3. Variations of EC (black line) and water levels above sea level (dashed gray line) as a result of tidal movements during five consecutive days. The monitoring station was located in a tributary of the Hau River in an area characterized for its intensive urbanized/industrial activities. The distance from the monitoring station to the Hau River was approximately 100 m. Note the inverse relationship between water- and EC levels.

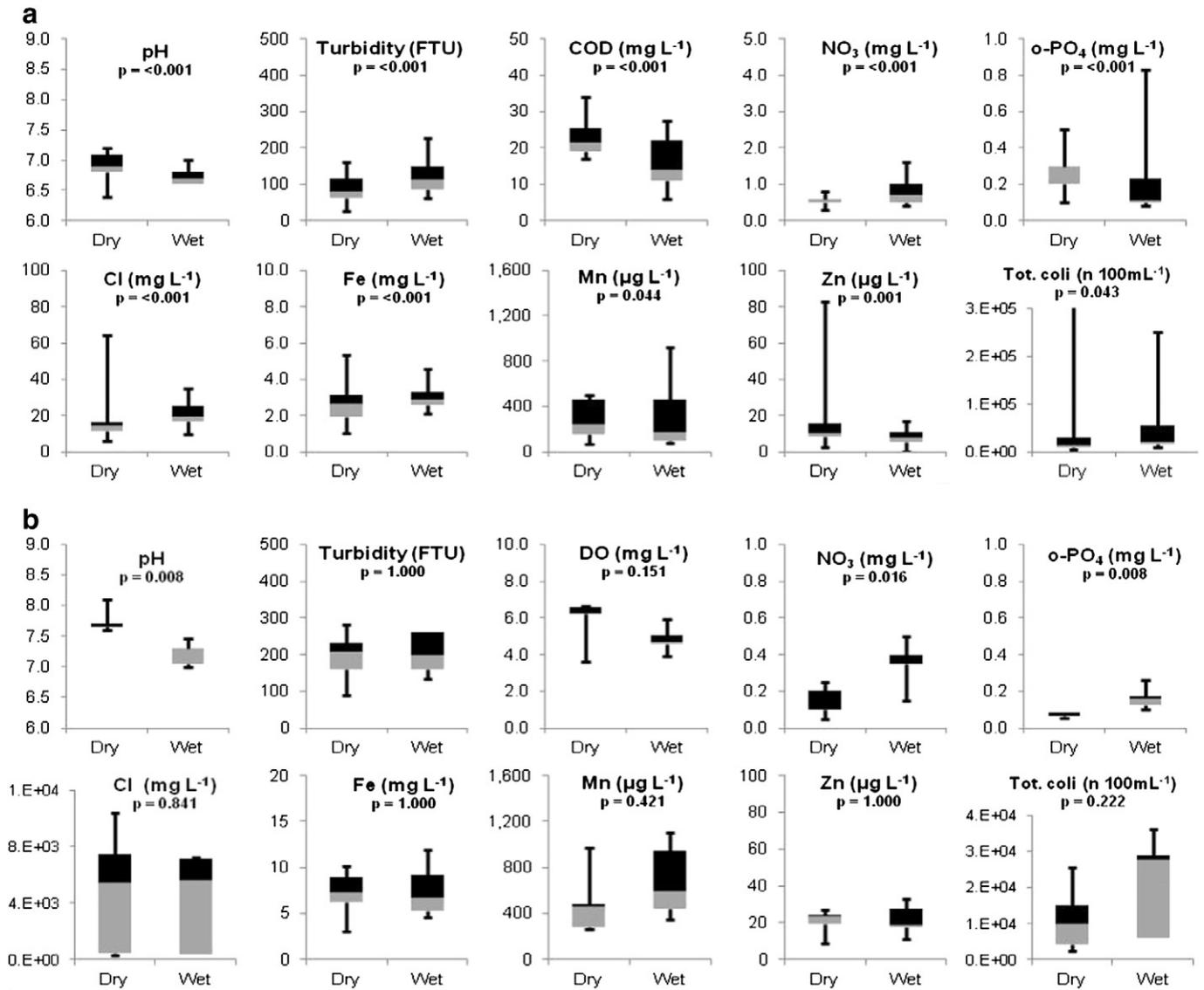
In the coastal region, however, the differences in turbidity and Fe concentrations between seasons were less pronounced. This could be explained by consistently strong flow velocities compared to the inland regions that cause a continuous erosion of soils regardless of season. The significantly higher Cl concentrations during the wet season at the inland regions could be caused by discharge water from rice fields in the early wet season. During the dry season, salts are accumulated in soil and flushed during the first rainfall events. In contrast, Cl concentrations did not significantly differ between seasons in the coastal region most probably due to continuous sea water intrusion. For nutrients,  $\text{NO}_3$  showed the highest concentrations during the wet season in both regions while  $\text{NH}_4$  concentrations did not vary at all. In contrast, Stärz (2012) found the highest concentrations for  $\text{NO}_3$  and  $\text{NH}_4$  during the dry season in two districts of the MD. The concentrations of o- $\text{PO}_4$  were significantly lower in the wet season for the inland regions although an opposite pattern is visible for the coastal region. These findings suggest that nutrient concentrations vary per location and/or per year. This is especially true for the nutrients, since small changes in the hydrology and/or land-use systems between locations and time can severely disturb the pattern of these substances. The concentrations of Mn were significantly higher during the dry season at the inland region but this pattern was not visible in the coastal region. Similar patterns are visible for the concentrations of COD and Zn. Lower DO concentrations were visible during the dry season in the inland regions (median concentrations:  $1.2 \text{ mg L}^{-1}$  and  $2.2 \text{ mg L}^{-1}$  at dry and wet seasons respectively for inland regions). This could be explained by a decreased dilution of waste water effluents during the dry seasons which results in the accumulation of pollutants. This finding is in line with the PCA which revealed that Mn and COD accumulate in waterways that lack mixing with fresh water during tidal regime. In the coastal area, this pattern was however not observed most probably due to a strong interaction between canal and sea water all year round.

In general, the concentrations of most water quality parameters differ only slightly between seasons although significant differences were observed. Furthermore, seasonality does not lead to a shift in guideline exceedance for any water quality parameters. During the dry season, water levels and flow velocities are low which result in an accumulation of pollutants from particular point sources. In the wet season, these point source emissions are diluted by monsoonal rainfall events. However, such rainfall events increase the run-off from urban and agricultural lands which also contains pollutants. These counteracting mechanisms could explain the relatively small differences in surface water quality between the seasons. This finding is in contradiction with various studies to the effects of seasonality and water quality. Cenci and Martin (2004) for example found that trace metal concentrations in the Bassac River were twice as high in March (dry season) compared to October (wet season). A study in the United States on seasonal effects on water quality found that one water quality parameter can be a significant pollutant in one season and may not be important for another season (Ouyang et al., 2006). Thus, seasonal effects on water quality seem to be small in secondary canals of the MD in comparison with other waterways and regions.

### 3.4. Hot-spot areas of pollution

#### 3.4.1. Spatial visualization

Surface water quality was found to be related to soil type, land-use and mixing of water by the tidal regime (river distance) (see also Supplementary data S1.1, S1.2 and S1.3). Based on these relationships, regression models were developed to predict and visualize surface water quality for one selected general parameter (DO), two nutrients (o- $\text{PO}_4$ ,  $\text{NH}_4$ ), one metal (Mn) and an indicator for microbial pollution (total coliforms). The selected parameters were chosen for their strong relationship with either land-use and/or river distance. Most other substances with significant correlations with either land-use and/or river distance showed lower  $R^2$  values ( $<0.60$ ), which indicates that other



**Fig. 4.** Differences of selected water quality parameters between seasons visualized by box-and-whisker diagrams for a) the inland locations at Can Tho/Hau Giang provinces (based on 27 locations) and b) the coastal region in Soc Trang province (based on 5 locations). The boxes represent from bottom to top: minimum, 25th percentile, median, 75th percentile and maximum values derived from the measurements within the selected regions. Note the differences in concentration range ( $\text{NO}_3$ , Cl, Fe, total coliforms) and significance ( $p$ ) between the regions. Dissolved oxygen (DO) was selected instead of COD in the coastal region due to high salinity of which interfered with COD measurements.

factors explain their presence in the surface waters of the MD and were therefore not included in this regression analysis. Earth metals were also not selected for regression since detailed soil maps were not available. Regression modeling was only performed for the inland regions (Table 2).

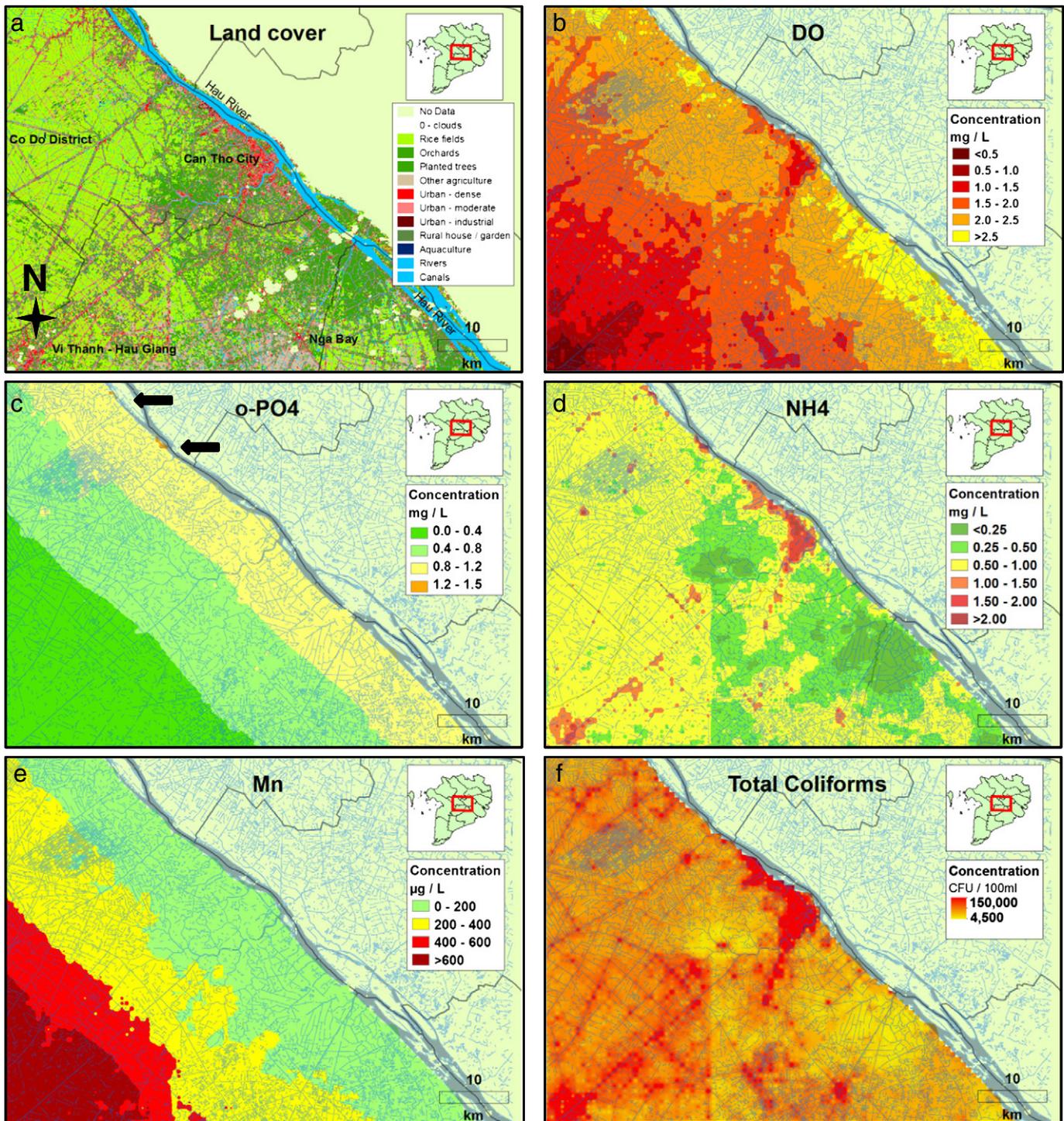
The regression models predict 68% ( $\text{o-PO}_4$ ) to 89% ( $\text{NH}_4$ ) of the variance in the presence of the selected substances in surface water. Aquaculture was the strongest predictor for  $\text{NH}_4$  and  $\text{o-PO}_4$  whereas distance to rivers had a very strong influence on the concentrations of DO and Mn. Urbanization was the strongest predictor for total coliform

concentrations. The regression models of the selected water quality parameters were used to generate surface water quality maps to identify hot-spot areas of pollution (Fig. 5). The maps are based on annual median concentrations of pollutants as determined in water samples collected during outgoing tide. The water quality maps only represent expected concentrations in secondary canals. Thus, pollutant concentrations in primary- and main waterways may be different from those presented in the maps. Besides land-use and distance to rivers, many other parameters could also impact the water quality such as elevation, differences in precipitation between

**Table 2**

Regression formulas for selected water quality parameters at inland locations (Can Tho and Hau Giang provinces).

| Parameters      | F-value | p     | R <sup>2</sup> | Regression formula  |
|-----------------|---------|-------|----------------|---|
| DO              | 38.9    | <0.01 | 0.82           | $2.82 - (0.04\text{RiverDist.}) - (0.02\text{Urbanization})$                                    |
| $\text{o-PO}_4$ | 18.3    | <0.01 | 0.68           | $10^{-0.512 + (0.029\text{Aquaculture}) - (0.014\text{RiverDist.})}$                            |
| $\text{NH}_4$   | 41.9    | <0.01 | 0.89           | $10^{-0.248 + (0.008\text{Urbanization}) - (0.010\text{Orchards}) + (0.038\text{Aquaculture})}$ |
| Mn              | 55.4    | <0.01 | 0.87           | $10^{2.109 + (0.022\text{RiverDist.}) - (0.006\text{Orchards})}$                                |
| Total coliforms | 22.9    | <0.01 | 0.73           | $10^{4.137 - (0.005\text{Orchards}) + (0.013\text{Urbanization})}$                              |



**Fig. 5.** (a) Land cover map of the inland region of the Mekong Delta (Can Tho and Hau Giang provinces) (data: Huth et al., 2012); annual median concentrations visualized by regression models based on significant correlations with land-use and/or river distance for (b) dissolved oxygen, (c) ortho-phosphate, (d) ammonium, (e) manganese and (f) total coliforms in the secondary canals of the selected region. The blue lines in the background indicate the dense network of artificially constructed secondary waterways and show the expected water quality at a given canal. The blue area in the northwestern part of the maps indicates a frequently flooded area. Due to different hydrological situations and the absence of measurement locations in the northeastern part above the main river, this area was not included for regression and is shown with a light green color. Resolution of maps: 750 m.

sites, density of canals and impact of artificial water works like dykes and sluice gates on the refreshment rate from tides. However, these parameters were not included in the regression analysis since accurate and/or digital data was not available of these parameters to assess their actual impact on water quality. It is however recommended to

further investigate the effects of these parameters on surface water quality as they could be important predictors for water quality as well.

The lowest DO concentrations (Fig. 5b) are visible at the furthest locations from the Hau River. This pattern could be explained by the continuous accumulation of organic pollutants at locations further

away from main rivers that reduce the available oxygen in surface water as a result of biological degradation. In some cases, this leads to almost anoxic conditions. However, low DO concentrations are also dependent on the level of urbanization. An example of low oxygen concentrations is visible within Can Tho City as well as in other urbanized areas. The highest concentrations of o-PO<sub>4</sub> are visible next to fish farms near the Hau River (indicated with black arrows) with observed concentrations of 1.5 mg L<sup>-1</sup> (Fig. 5c). Lowest o-PO<sub>4</sub> concentrations are visible at locations far away from the Hau River. The pattern of lower o-PO<sub>4</sub> concentrations at these locations could be explained by elevated organic pollution at locations further away from the rivers that potentially adsorb the available o-PO<sub>4</sub> in water. Although at some locations high concentrations of o-PO<sub>4</sub> were observed (see peak concentrations near arrows in Fig. 5c due to aquaculture), algae blooms were not detected in the surface waters of the MD which could be explained by the high turbidity levels that reduce the penetration of sunlight. The lowest NH<sub>4</sub> concentrations (Fig. 5d) are visible in areas that contain high densities of orchards (<0.50 mg L<sup>-1</sup>). However, the majority of the map shows concentrations above 0.50 mg L<sup>-1</sup> which are areas generally dominated by rice fields. The observed peaks with concentrations of up to >2 mg L<sup>-1</sup> are visible at urbanized locations like Can Tho City and fish farms which are visible as small orange to red dots on the map. This finding is particularly relevant for water supply companies since NH<sub>4</sub> concentrations >0.50 mg L<sup>-1</sup> could severely affect the disinfection efficiency by chemical treatment such as chlorination (EU, 1998). The concentrations of Mn (Fig. 5e) are strongly related to the distance to main rivers with the concentration of concerns in these areas. These high concentrations are in line with PCA which also indicated the accumulation of this metal in surface water where mixing with fresh water is reduced. The concentrations of total coliforms (Fig. 5f) are, similar to that of NH<sub>4</sub>, being lowest in orchard dominated areas although drinking water guideline values are exceeded at all locations. Nevertheless, large differences are visible in total coliform concentrations with the highest observed values within urbanized areas as well as along main infrastructures such as main roads that also contain high densities of houses.

These findings are especially relevant to policy makers to detect hot-spot areas of pollution and to develop water management strategies. The presented maps could also be of interest for water supply and ice-producing companies to define treatment systems and optimal locations for water extraction. The presented surface water quality maps are especially designed for such practitioners since they are easier to understand than correlation tables and regression formulas.

### 3.4.2. Validation

Data from 20 measurement locations were used to develop regression models and surface water quality maps. In order to assess the accuracy of water quality predictions in other areas, the modeled concentrations were validated with observed concentrations at three independent locations. Validation points were selected at

locations that represented various land-use systems and different distances to main rivers (Table 3).

Location Cai Da, representing the land use mix "urbanization/orchards", showed that DO and NH<sub>4</sub> concentrations were predicted within the validation range although observed concentrations were close to the lower modeled boundary. This validation data point (Stärz, 2012) was collected in 2008 which could have slightly different climatologic and/or land-use conditions in comparison with our measurements in 2011/2012. The observed measurements in Hoa An, representing rice fields and a river distance of >30 km, fitted well with the modeled values. The validation location Co Do, representing rice fields and aquaculture, showed two observed measurement concentrations above the modeled values (NH<sub>4</sub> and o-PO<sub>4</sub>). This finding highlights the uncertainty of modeling surface water quality around small but heavily polluting point sources such as (fish) farms due to a large variation in the hydrology of canals as well as variability in the emissions. In summary, the regression models generally predict surface water quality within the validation range (95% confidence interval) except occasionally, for local point sources such as fish farms. These water quality maps should be used as a first screening to get an indication of the likelihood of pollution at specific locations. However, recent water quality measurements are required when the actual water quality is needed at a specific location due to strong variation in local hydrology and the potentially strong influences of point sources.

## 4. Conclusions

Secondary canals are intensively used by local populations for both drinking and domestic services. The quality of these waters is generally poor, especially compared to main water systems such as rivers. Thus the usage of this water can lead to severe health concerns, particularly near point sources (fish farms) and within industrial/urbanized agglomerations. Most water quality monitoring campaigns in the MD focus on main canals and rivers. Due to the intensive use and pollution of secondary canals it is therefore recommended to set-up spatially-explicit water management strategies to monitor and improve the local water quality at different time intervals. Furthermore, educational programs should be organized to inform local populations about the risks of using surface water and the effective water treatments to improve its quality. Households should also be encouraged to use surface water only during incoming tide since the quality is better compared to outgoing tides. However, people that live within a close distance to main sources of pollution (fish farms, industrial areas, large villages, cities) should be discouraged to use surface water from secondary canals at all and alternative water supply facilities should be put in place by local authorities. Based on the water quality maps, hot-spot areas of pollution can be identified which is also relevant for drinking water companies to define ideal water extraction locations. Based on the results of this study, landscapes with predominantly fruit orchards seem to be promising locations since most investigated pollutant concentrations were low in these areas, although screening for pesticides from these systems should also be considered.

**Table 3**

Validation of the regression models by comparing modeled annual median 95% confidence interval concentrations with observed annual median concentrations from three independent measurement locations. The bold numbers indicate when modeled concentrations did not meet the observed concentrations.

|   | Cai Da–Can Tho province <sup>a</sup> |             | Hoa an–Hau Giang <sup>b</sup> |              | Co Do–Can Tho province <sup>c</sup> |                  |
|---|--------------------------------------|-------------|-------------------------------|--------------|-------------------------------------|------------------|
|   | Observed <sup>d</sup>                | Modeled     | Observed                      | Modeled      | Observed                            | Modeled          |
| DO (mg L <sup>-1</sup> )                    | 2.2                                  | 1.9–2.7     | 0.8                           | 0.5–2.0      | 1.4                                 | 1.3–2.4          |
| o-PO <sub>4</sub> (mg L <sup>-1</sup> )     | –                                    | 0.20–0.39   | 0.10                          | 0.03–0.21    | 0.30                                | <b>0.08–0.29</b> |
| NH <sub>4</sub> (mg L <sup>-1</sup> )       | 0.25                                 | 0.25–0.94   | 0.60                          | 0.40–0.85    | 2.70                                | <b>0.45–0.99</b> |
| Mn (mg L <sup>-1</sup> )                    | –                                    | 78.3–163.6  | 582.8                         | 474.6–1730.9 | 459.0                               | 235.0–562.6      |
| Total coliforms (CFU 100 mL <sup>-1</sup> ) | –                                    | 7043–21,478 | 11,909                        | 8868–20,098  | 14,594                              | 10,204–20,008    |

<sup>a</sup> Validation point located in urbanized and orchard dominated areas.

<sup>b</sup> Validation point located in rice field dominated area at an inland location with low tidal movements.

<sup>c</sup> Validation point located in rice field and aquaculture dominated areas.

<sup>d</sup> Results are from Stärz (2012). PO<sub>4</sub>, total coliforms and Mn were not investigated in this study.

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## Appendix A. Supplementary data

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.scitotenv.2014.03.049>. These data include Google maps of the most important areas described in this article.

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