Chemosphere 88 (2012) 1083–1089

Contents lists available at SciVerse ScienceDirect

Chemosphere

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

Occurrence and behavior of emerging contaminants in surface water and a restored wetland

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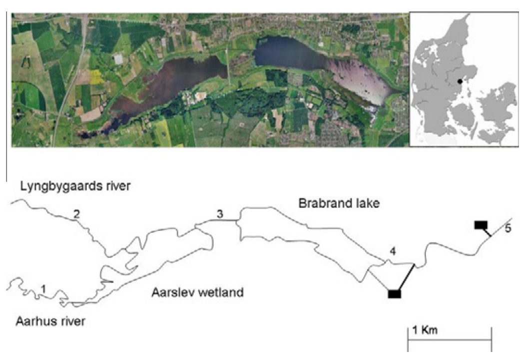
HIGHLIGHTS

- Occurrence of 17 emerging contaminants in Danish surface waters.
- Diclofenac, MCPA, caffeine, and TCEP were the most abundant.
- Attenuation capacity of the restored wetland ranged from no mitigation to 84%.
- PCA grouped samples by source pollution.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 13 December 2011
Received in revised form 2 April 2012
Accepted 22 April 2012
Available online 26 May 2012

Keywords:
Constructed wetland
PCPs
Pharmaceutical
Pesticide
Mitigation
Agricultural run-off

ABSTRACT

Pollution mitigation is an important target for restored wetlands, and although there is much information in relation to nutrient removal, little attention has been paid to emerging contaminants. This paper reports on the occurrence and attenuation capacity of 17 emerging contaminants in a restored wetland and two rivers in North-East Denmark. The compounds belong to the groups of pharmaceuticals, fragrances, antiseptics, fire retardants, pesticides, and plasticizers. Concentrations in surface waters ranged from 2 to 1476 ng L^{-1}. The compounds with the highest concentrations were diclofenac, 2-methyl-4-chlorophenoxyacetic acid (MCPA), caffeine, and tris(2-chloroethyl) phosphate (TCEP). The herbicide concentrations increased after a rain-fall event, demonstrating the agricultural run-off origin of these compounds, whereas the concentration of the other emerging contaminants was rather conservative. The mitigation capacity of the restored wetland for the compounds ranged from no attenuation to 84% attenuation (19% on average). Hence, restored wetlands may be considered as a feasible alternative for mitigating emerging contaminants from river waters.

1. Introduction

Emerging contaminants are a large, relatively new group of compounds that includes pharmaceuticals, personal care products (PCPs), plasticizers, surfactants, and pesticides, among others. The widespread occurrence of these contaminants in freshwater is potentially a major problem with consequences that are yet to be fully understood (Sharma et al., 2009; González et al., 2012). Conventional wastewater treatment plants (WWTPs) are not designed to remove emerging contaminants, and many of these compounds are therefore discharged into surface waters (Ternes et al., 2004; Pal et al., 2010). Although some of the compounds have been

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http://dx.doi.org/10.1016/j.chemosphere.2012.04.048

proposed to be included in regulatory lists (European Commission, 2006), there is relatively little information on their ecotoxicological effects, and until now they have escaped regulations (Murray et al., 2010). Known environmental effects of some of the emerging contaminants are the reduction of macroinvertebrate diversity in rivers (Muñoz et al., 2009) and behavioral changes in mosquito fish (Henry and Black, 2008).

The intensification of agriculture with high fertilization rates and use of pesticides has increased the discharge of nutrients and pollutants into the aquatic ecosystems. However, in some countries, discharge of nutrients from point sources such as WWTPs and industry still contributes significantly to riverine pollution loading (Kronvang et al., 2001). Enhanced levels of nutrients in aquatic ecosystems have led to increased primary production, and the consequences derived from this eutrophication are algal blooms, increased water turbidity, oxygen depletion, and fish deaths (Kalff, 2002). In order to reduce sediments, nutrients and pollutants entering streams, lakes, groundwaters, and coastal waters, several countries such as Sweden, Denmark and the USA, have created or restored wetlands with the aim to reinstall ecosystem services that were lost after wetlands were drained and converted into agricultural land (Mitsch et al., 2005; Hoffmann and Baattrup-Pedersen, 2007; Thiere et al., 2009; Hoffmann et al., 2011). The European Union (EU) member states have adopted the EU Water Framework Directive, which demands that a good ecological and chemical quality should be reached in water bodies by the end of 2015 (European Commission, 2000). On the national scale, the Danish Action Plans have set a national target of increasing the wetland area to reduce the annual nitrogen load to the sea (Hoffmann and Baattrup-Pedersen, 2007).

Wetlands have also received much attention in recent years due to their inherent capacity for removing pesticides, surfactant, PCPs, pharmaceuticals, and other microcontaminants (Schulz et al., 2003; Gross et al., 2004; Conkle et al., 2008; Matamoros and Bayona, 2008; Gregoire et al., 2009). Hence, wetlands offer important ecological benefits complying with the good chemical status demands by the EU framework directive (European Commission, 2000). Perhaps, constructed wetland systems (CWs) are the most well-known example of how wetlands can be used to attenuate pollution (e.g. Brix and Schierup, 1989). In CWs treating domestic wastewaters, emerging contaminants are reported to be eliminated by photodegradation, biodegradation, sedimentation, plant uptake and/or adsorption (Matamoros and Bayona, 2008). However, despite the demonstrated positive effect of CWs on the attenuation of emerging contaminants from wastewaters, little attention has been paid to the fate of emerging contaminants in natural, restored and created wetlands that are fed with natural waters impacted by urban and agricultural run-off.

The aim of this study is to assess the occurrence and mitigation capacity of emerging contaminants in a restored wetland system fed by two rivers impacted by urban and agricultural run-off. The targeted emerging contaminants are pharmaceuticals, fragrances, antiseptics, fire retardants, herbicides, and plasticizers. These compounds cover a wide range of polarity (log Dow from -2 to 6), biodegradability and photodegradability. The group of emerging contaminants considered was selected on the basis of their concentration and detection frequencies in surface waters (Murray et al., 2010; Calderón-Preciado et al., 2011).

2. Material and methods

2.1. Chemicals and reagents

Gas chromatography (GC) grade (Suprasolv) hexane, methanol, and ethyl acetate were obtained from Merck (Darmstadt, Germany). Analytical-grade hydrogen chloride was obtained from Panreac (Barcelona, Spain). Cashmeran, ibuprofen, 2-(methylthio)-benzothiazole, tributyl phosphate (TBP), methyl dihydrojasmonate, tris(2-chloroethyl) phosphate (TCEP), caffeine, galaxolide, tonalide, carbamazepine, naproxen, bisphenol A, triclosan, ketoprofen, diclofenac, furosemide, mecoprop, 2-methyl-4-chlorophenoxyacetic acid (MCPA), 2,2′-dinitrophenyl, and dihydrocarbamazepine were purchased from Sigma-Aldrich (Steinheim, Germany). 2,4,5- Trichlorophenoxypropionic acid (2,4,5-TPA) was from Reidel-de-Haen (Seelze, Germany). Trimethylsulfonium hydroxide (TMSH) was from Fluka (Buchs, Switzerland). Strata-X polymeric SPE cartridges (200 mg) were from Phenomenex (Torrance, CA, USA) and the 0.7 μm glass fibre filters of ∅ = 47 mm were from Whatman (Maidstone, UK).

2.2. Sampling site description

The study area is located to the west of the city of Aarhus, Denmark (56°08′ N, 10°04′ E). It consists of two feeding rivers, the restored wetland (Aarslev), a lake (Brabrand) and a discharge channel, all of which lie in a sub-glacial stream trench. The restored wetland and the lake are interconnected by the Aarhus river (restored wetland outlet). The study basin extends over an area of 250 km^2 and is drained by the two rivers which flow into the restored wetland and the lake (Fig. 1). The basin is underlain by fluvio-glacial sandy loams, and the mean annual precipitation in the basin is approx. 650 mm. The two main rivers, the Aarhus river (watershed 120 km^2) and the Lyngbygaards river (watershed 132 km^2), drain the basin which consists predominantly of arable land with small villages and dwellings. The restored wetland, Aarslev (100 ha) was created in 2003 to reduce the nutrient input to Brabrand lake and the coastal waters downstream. The wetland was restored by dismantling drainage pumps, removing drainage canals and by diverting water from Aarhus river and Lyngbygaards river into the former agricultural area. The restoration resulted in the creation of a new shallow wetland with an average water depth of 0.50 m and a maximum depth of 2 m. Lake Brabrand (153 ha) is located downstream from the restored wetland and has an average water depth of 0.85 m, a maximum depth of 2.7 m, and is surrounded by a dense littoral zone with reeds (mostly *Phragmites australis, Schoenoplectus lacustris* and *Typha latifolia*) and wet meadows. During the summer, patches of the restored wetland are covered by floating islands of water-lilies (*Nymphaea alba*) and bulrushes (*S. lacustris*). Average hydraulic flow rates were 0.96 and 1.03 $m^3 s^{-1}$ for the Aarhus river and Lyngbygaards river respectively. Hydraulic residence time in the restored wetland ranged between 3 and 20 d over the year (average 7 d) and in Lake Brabrand between 5 and 25 d (average 12 d). The Aarhus and Lyngbygaards rivers are subjected to important anthropogenic discharges by the WWTPs located upstream of the sampling points. The Brabrand lake system is important since some of the city's water supply wells are located near the lake and the lake is a popular local recreational site.

2.3. Sampling strategy

Sampling was performed from September to December 2010 (29/09; 13/10; 26/10; 10/11; 2/12; 15/12). The sampling locations included both rivers, the restored wetland outlet, lake Brabrand outlet and the discharge from the system, Aarhus channel (Fig. 1). Sampling sites were selected to assess the attenuation capacity of the restored wetland. In total, 29 water samples were taken. All samples were collected in 1000 mL clean amber glass bottles, which were transported under refrigeration to the laboratory where they were stored at 4 °C until analysis. The sample holding time was less than 12 h.

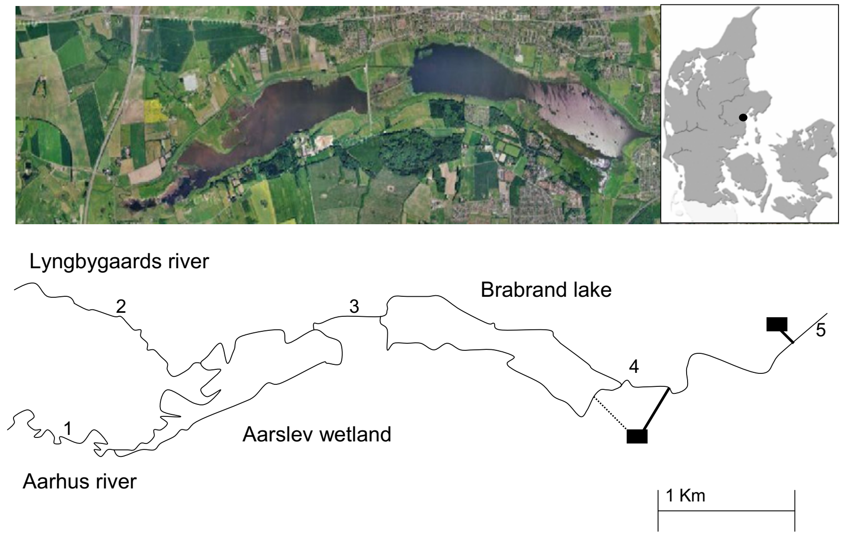

Fig. 1. Map of Denmark representative of the sampling sites studied (1. Aarhus river, 2. Lyngbygaards river, 3. Restored wetland outlet, 4. Brabrand outlet, and 5. Aarhus channel). Black boxes represent the WWTPs (from Google earth).

2.4. Analytical methodology

All water samples were filtered and processed as previously reported by Matamoros and Bayona (2006). Briefly, a sample volume of 1000 mL was spiked with 1 μg of a surrogate standard (2,2′-dinitrophenyl, dihydrocarbamazepine, and 2,4,5-TPA). The spiked sample was percolated through a previously activated polymeric solid-phase extraction cartridge (200 mg Strata X). Elution was performed with 10 mL of hexane/ethyl acetate (1:1). The eluted extract was evaporated until ca. 100 μL under a gentle N_2 stream, and 186 ng of triphenylamine was added as an internal standard. Finally, the vial was reconstituted to 300 μL with ethyl acetate.

Methylation of the acidic carboxyl group was performed in a hot GC injector (270 °C) by adding 10 μL of TMSH solution (0.25 M in methanol) to a 50 μL sample before injection. Derivatised samples were injected into a Shimadzu GC–MS 2010 (Shimadzu Corporation, Japan) in the electron impact mode (70 eV ionization energy) fitted with a 30 m × 0.25 mm id, 0.25 μm film thickness TRB5-MS coated with 5% diphenyl 95% dimethylpolysiloxane from Teknokroma (Sant Cugat del Vallès, Spain). 1 μL of the sample was injected in the splitless mode. Chromatographic conditions, data processing and validation of the methodology have been described elsewhere (Matamoros and Bayona, 2006; Matamoros et al., 2010). Acquisition was performed in selected-ion monitoring mode at 2 scans s^{-1}. The limit of detection (LOD) and limit of quantification (LOQ) of the analytical methodology were determined (using Milli-Q water) from the mean of the background noise plus 3 or 10 times the standard deviation of the background noise, respectively. LOD and LOQ ranged from 2 to 40 ng L^{-1} and from 4 to 60 ng L^{-1}, respectively. Recoveries and repeatability were always higher than 90% and lower than 20%.

2.5. Statistical analysis

Principal component analysis (PCA) (Jolliffe, 1986; Peré-Trepat et al., 2006) was performed on the data set using the SPSS v.15 package (Chicago, IL). Concentration values were obtained from Table 1. Data were arranged in a matrix in which sample concentrations were represented in rows, and target analytes (17) were in columns; samples were further arranged by sampling site and time. Before the application of PCA, concentration values below the LOQ were set to half their limit of quantification. Once the data matrix was completed, it was autoscaled to have zero mean and unit variance (correlation matrix) in order to avoid problems arising from different measurement scales and numerical ranges of the original variables (Helena et al., 2000; Hildebrandt et al., 2008). A comparison of means was conducted by the paired samples t-test.

3. Results and discussion

3.1. Occurrence of emerging contaminants

The Aarhus channel sampling site exhibited the largest overall frequency of detection and concentration (94%, 4.4 μg L^{-1}) followed by the Aarhus river (88%, 4.3 μg L^{-1}), the Lyngbygaards river (83%, 2.7 μg L^{-1}), the restored wetland outlet (80%, 2.7 μg L^{-1}) and finally the Brabrand lake outlet (66%, 3.0 μg L^{-1}). These results indicate that the Aarhus channel is highly impacted by the discharge from two WWTPs (Fig. 1), that the Aarhus river is the most significant source of pollution, and that the restored wetland system enables the attenuation of certain emerging contaminants.

The concentration of emerging contaminants in water samples ranged from 3 to 1472 ng L^{-1} (Table 1). Diclofenac, MCPA, caffeine, and TCEP were the most abundant (>50 ng L^{-1}, on average). This agrees with earlier reports of diclofenac and TCEP being the most recalcitrant contaminants in conventional activated sludge WWTPs (Heberer, 2002; Miège et al., 2009) and consequently the most abundant in surface waters impacted by WWTPs (Reemtsma et al., 2008; Pal et al., 2010). The high abundance of caffeine cannot be attributed to its recalcitrance, as elimination efficiencies of over 90% is common in conventional WWTPs (Carballa et al., 2005). Hence, the abundance of caffeine is probably due to the high concentration of caffeine observed in raw wastewater as a consequence of the coffee consumption (Matamoros et al., 2007). The high abundance of MCPA was apparently caused by agricultural run-off in the watershed since this herbicide is largely used in farming (Felding, 1995). Levels of emerging contaminants found in this study are generally in good agreement with levels reported in other studies (Moldovan, 2006; Pal et al., 2010).

Ketoprofen and triclosan were detected most frequently in the Aarhus channel, which is consistent with the wastewater discharges at this point. Ketoprofen and triclosan were low or not detected at the other sampling sites, probably due to their high reported photodegradation rates (half-lives from 2 min to 4–8 d)

Table 1
Frequency of detection (FOD), minimum, maximum (in brackets) and mean concentration of the 17 emerging contaminants in the five sampling sites.

	Aarhus river		Lyngbygaards river		Restored wetland outlet		Brabrand lake outlet		Aarhus channel	
	FOD[a]	Conc. (ng L^{-1}) (min–max) mean	FOD	Conc. (ng L^{-1}) (min–max) mean	FOD	Conc. (ng L^{-1}) (min–max) mean	FOD	Conc. (ng L^{-1}) (min–max) mean	FOD	Conc. (ng L^{-1}) (min–max) mean
Cashmeran	2/6	(3–3)3	2/6	(4–5)4	0/6	<2	0/5	<2	2/6	(4–9)7
Ibuprofen	6/6	(9–21)14	6/6	(9–22)14	6/6	(8–18)13	5/5	(8–25)14	6/6	(14–32)20
Mecoprop	5/6	(13–21)16	6/6	(13–15)14	6/6	(13–15)14	5/5	(13–17)15	6/6	(16–24)19
MCPA	6/6	(45–1475)311	6/6	(16–166)52	6/6	(29–303) 133	5/5	(29–232) 121	6/6	(35–247) 138
TBP	5/6	(20–28)24	4/6	(18–25)22	5/6	(18–24)22	5/5	(19–26)23	6/6	(30–44)35
Methyl dihydrojasmonate	6/6	(27–51)41	5/6	(22–66)34	5/6	(22–32)27	5/5	(23–34)29	6/6	(22–42)39
TCEP	6/6	(46–80)58	6/6	(40–91)53	6/6	(40–55)48	5/5	(42–55)50	6/6	(53–94)70
Caffeine	6/6	(126–214) 167	6/6	(65–382) 212	6/6	(101–273) 176	5/5	(117–238) 195	6/6	(153–349) 237
Galaxolide	6/6	(23–57)34	6/6	(15–28)22	6/6	(10–24)18	4/5	(13–42)23	6/6	(44–72)59
Tonalide	6/6	(9–13)10	5/6	(8–10)9	5/6	(8–9)8	4/5	(8–12)9	6/6	(13–99) 34
Carbamazepine	6/6	(17–36)27	6/6	(12–38)20	6/6	(12–39)22	5/5	(12–45)24	6/6	(23–95)50
Naproxen	6/6	(16–31)21	6/6	(17–36)26	6/6	(17–25)21	5/5	(15–28)21	6/6	(25–34)31
Bisphenol A	4/6	(4–31)13	1/6	5	3/6	(5–46)18	2/5	(4–8)6	1/6	10
Triclosan	5/6	(4–17)7	2/6	(10–60)35	1/6	22	2/5	(8–8)8	6/6	(4–16)8
Ketoprofen	0/6	<6	0/6	<6	0/6	<6	0/5	<6	5/6	(31–62)41
Diclofenac	6/6	(35–71)53	6/6	(32–71)49	6/6	(45–61)51	5/5	(39–156) 71	6/6	(80–134) 96
Furosemide	3/6	(27–79)46	4/6	(16–35)27	3/6	(16–19)17	0/5	<12	3/6	(17–38)26

[a] Number of samples with concentration > LOD/total number of samples.

in surface waters (Boreen et al., 2003; Aranami and Readman, 2007). In the case of triclosan, sorption into the organic matter present in the wetland cannot abstracted due to its hydrophobicity (log Kow = 4.76).

3.2. Temporal trend

The temporal dynamics of concentrations at the five sampling sites are illustrated for herbicides, pharmaceuticals, PCPs, and other compounds in Fig. 2. The concentration of herbicides at each sampling site exhibited high variability whereas concentrations of pharmaceuticals were rather comparable throughout the sampling period. These differences may be accounted for by the continual use of pharmaceuticals and PCPs, and their consequent release from the WWTPs rather than by seasonal patterns in the application of herbicides (Matamoros et al., 2008).

The concentrations of pharmaceutical compounds and PCPs were higher in the inlet river waters than in the outlets from the restored wetland and Brabrand lake, presumably due to the capacity of the wetlands for removing these compounds. However, the Aarhus channel had higher concentrations of these compounds, apparently due to the discharge from two WWTPs between the Brabrand lake effluent and the Arhus channel sampling site (Fig. 1).

The highest herbicide concentrations observed during the sampling campaign carried out on the 26th October 2010 may be explained by a heavy rainfall episode that occurred during the previous days (48-h accumulated precipitation exceeded 24 mm, Danish Metereological Institute). As it can be seen from Fig. 2, the Aarhus river showed the highest concentration of herbicides. Herbicide application on farmlands and consequent run-off into the Aarhus river drainage basin is the most likely explanation for the high herbicide concentrations in Aarhus river. The individual concentration of herbicides (i.e. MCPA) from September to November was higher than 0.1 μg L^{-1}, which is the maximum limit for drinking water in Europe (Council of the European Union, 1998), but the concentration was lower in December. These results suggest that the presence of snow and ice on agricultural fields during December may reduce agricultural run-off.

Our measurements of emerging pollutants suggest that water should not be abstracted from the drinking extraction wells located at Aarslev wetland and lake Brabrand, as it has been observed that some of these compounds move easily through groundwater (Buss et al., 2006; Carrara et al., 2008). In fact, Liu et al. (2007) determined that phenoxy acid herbicides were present in groundwater samples from an old pumping site in Denmark with concentrations up to 5800 μg L^{-1}.

3.3. PCA analysis

To get further understanding of the occurrence and behavior of contaminants in the studied system a PCA was performed. The contribution of each variable to every principal component, PC, is shown in Table 2. Moreover, the explained variance by component is also included. The first five PCs, which explain 76% of the variance contained in the original data set, had an eigenvalue of greater than one. The first principal compound (PC 1) accounted for 32%, whereas the second, third, fourth and fifth compound accounted for 16%, 12%, 10% and 6%, respectively. However, when a complex system such as this one is studied, it is hard to identify the underlying variables in the final PCs. Therefore, we have only retained the first three, which altogether explained 59% of the total variance.

The first PC had high positive loadings for most of the emerging contaminants indicating a similar origin of these compounds. The positive loading of these compounds correlates with their high abundance in the Aarhus channel, and suggests that the discharge of emerging contaminants from the WWTPs affects this component. The second PC had positive loading for cashmeran, TCEP, carbamazepine and bisphenol A, whereas it had negative loadings for ibuprofen, caffeine, tonalide and triclosan. PC 2 describes the temporal variability, with positive contributions for compounds with high abundance in the September and October campaigns, and negative contributions for compounds with the highest abundance during the November and December campaigns. The third PC had high loadings for MCPA, methyl dihydrojasmonate, bisphenol A and triclosan indicating that, in addition to other possible factors, agricultural run-off is associated with this PC.

Fig. 3 illustrates the scores plots for PC1 *vs.* PC2. The most relevant cluster included samples with low score values for both PC1 and PC2. Samples with low abundance of emerging contaminants (negative score values of PC1) showed low temporal concentration variability (low score values of PC 2), whereas samples with high

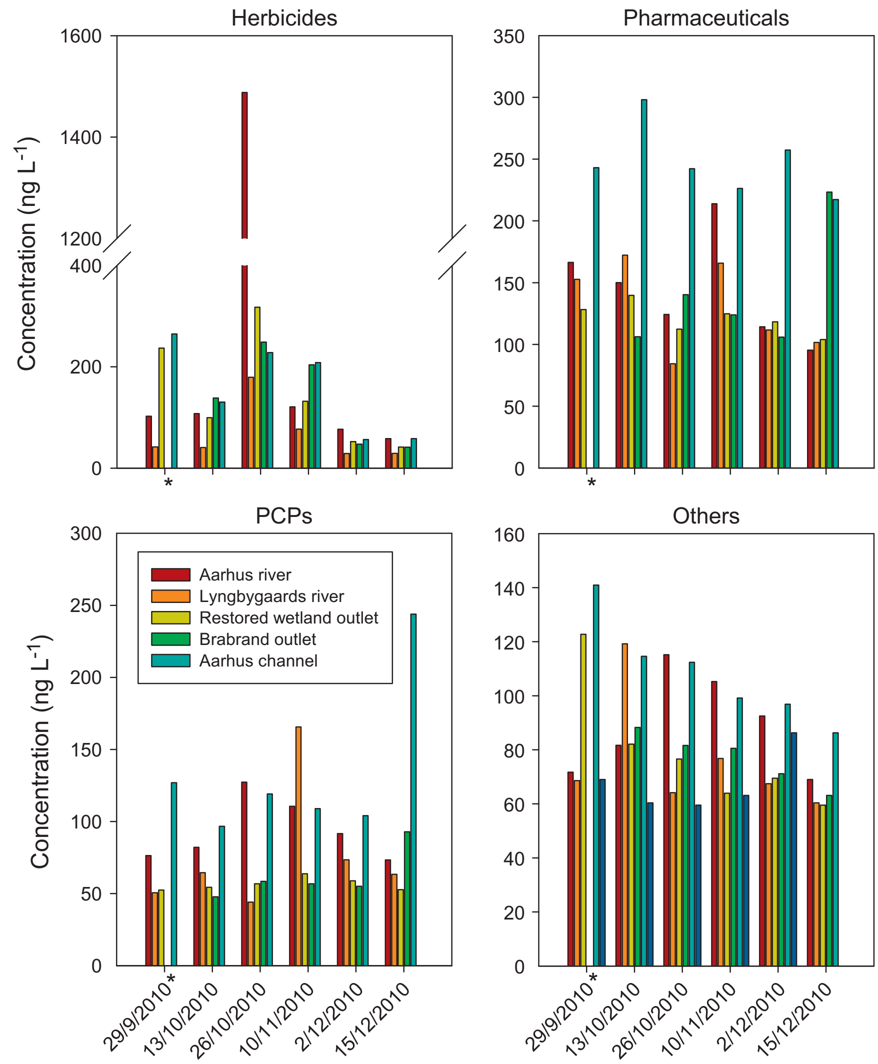

Fig. 2. Temporal and spatial variability of emerging contaminants grouped as herbicides (mecoprop and MCPA), pharmaceuticals (ibuprofen, caffeine, carbamazepine, naproxen, ketoprofen, diclofenac and furosemide), PCPs (cashmeran, methyl dihydrojasmonate, galaxolide, tonalide, and triclosan), and others (2-(methylthio)-benzothiazole, tributyl phosphate, tri(2-chloroethyl) phosphate, and bisphenol A). *not analyzed.

abundance were not grouped in PC2, showing a variable temporal trend.

In the PC1 *vs.* PC3 scores plot, three main groups are distinguished. The most noticeable group includes the six samples from the Aarhus channel. These samples had high positive values for PC1 and low values for PC3, which indicates that they were very contaminated by emerging contaminants discharged from WWTPs, and not from herbicides from agricultural-run off. A second cluster included samples with a high value of PC3. The presence of samples with high concentration of MCPA in this cluster indicates a punctual contamination of herbicides, as these samples were collected during the rainfall event. Finally, the third cluster included samples with low values for both PC1 and PC3, indicating a low effect of WWTP discharge and agricultural run-off.

Overall, once a data set is obtained by successive monitoring campaigns, PCA is a useful tool to assess the origin and temporal contamination patterns. Samples with low abundance were shown to be associated with the low temporal variability, whereas samples with high agricultural run-off influence were correlated with a moderate abundance of emerging contaminants.

Table 2
Principal components analysis of the 17 selected variables (contaminants) at five sampling sites. Loadings for the three principal components are shown[a].

Name	PC1 (32%)	PC2 (16%)	PC3 (11%)
Cashmeran	0.396	**0.606**	−0.240
Ibuprofen	0.581	**−0.601**	0.158
Mecoprop	**0.792**	0.105	0.097
MCPA	0.059	0.295	**0.638**
TBP	**0.841**	0.339	0.001
Methyl dihydrojasmonate	0.168	−0.061	**0.835**
TCEP	**0.644**	**0.579**	0.093
Caffeine	0.355	**−0.588**	−0.051
Galaxolide	**0.882**	−0.019	0.021
Tonalide	0.501	−0.482	−0.132
Carbamazepine	0.534	**0.566**	−0.078
Naproxen	**0.766**	−0.359	0.016
Bisphenol A	−0.166	0.325	**0.520**
Triclosan	0.239	**−0.484**	**0.497**
Ketoprofen	**0.739**	−0.192	−0.222
Diclofenac	**0.675**	0.113	−0.212
Furosemide	0.204	0.173	0.279

[a] Variables with high loadings are shown in boldface type.

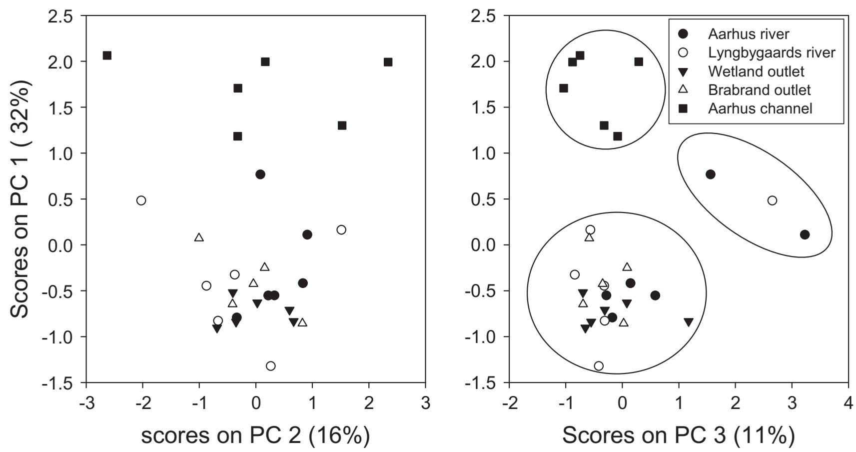

Fig. 3. Score plots for the first three components. The different symbols represent different sampling sites.

3.4. Mitigation capacity

A tentative mitigation capacity of the restored wetland taken into account the hydraulic flow rates was evaluated through the following equation

$$\text{Mitigation \_ efficiency} = \frac{1}{n}\sum_{i=1}^{n}\left(\frac{(C_{a_c} \times \text{Flow\_rate}_a + C_{b_c} \times \text{Flow\_rate}_b) - C_{\text{outlet}_c} \times \text{Flow\_rate}_{\text{outlet}}}{(C_{a_c} \times \text{Flow\_rate}_a + C_{b_c} \times \text{Flow\_rate}_b)}\right) \times 100 \quad (1)$$

where C_a, C_b and C_{outlet}, and Flow_rate_a, Flow_rate_b and $\text{Flow\_rate}_{\text{outlet}}$ are the concentrations of the specific compound and flow rates at the Aarhus river, the Lyngbygårds river, and the outlet of the restored wetland, respectively. The lowercase n represents each sampling campaign from 1 to 6. The flow rate data from each sampling site (Aarhus river, Lyngbygaards river and restored wetland outlet) provided by Aarhus municipality, were used to calculate the mitigation efficiency of the restored wetland.

Fig. 4 shows that the mitigation efficiency of each individual compound in the restored wetland ranged from no attenuation to 84%. The emerging contaminants were classified according to the ease by which they were eliminated by the restored wetland-lake system: (i) >40% (i.e. triclosan and furosemide); (ii) between 15% and 40% (i.e. cashmeran, methyl dihydrojasmonate, MCPA, galaxolilde, tonalide, and bisphenol A); and, finally, (iii) <15% (ibuprofen, mecoprop, tributyl phosphate, carbamazepine, naproxen, diclofenac, and TCEP).

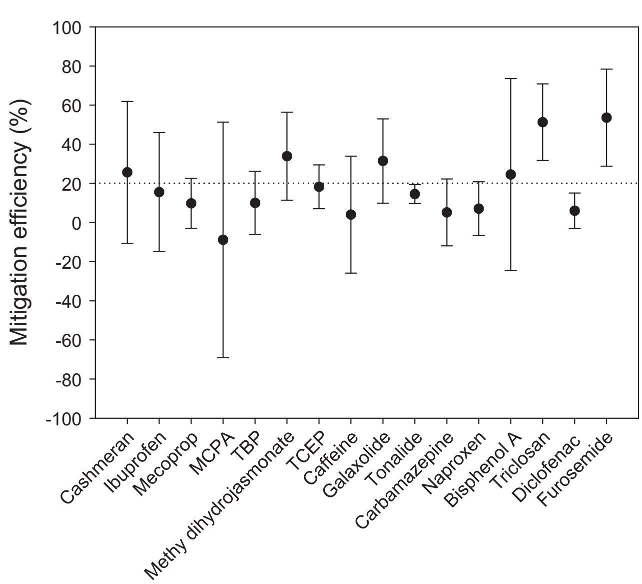

Fig. 4. Average mitigation efficiency of the emerging contaminants in the restored wetland (standard deviation is shown). Dotted line shows the overall average mitigation (19%).

Despite the simultaneous occurrence of biodegradation, sorption and photodegradation processes in the restored wetland, the average removal efficiency of all selected compounds was low and highly variable (19 ± 17%). This variability may be caused by the effects of water residence time in the restored wetland on corresponding influent and effluent concentrations which occasionally may lead to removal values of less than zero. But the low sun-light radiation and the cold conditions during the winter sampling campaigns may also have reduced the removal processes (Matamoros et al., 2008). The vegetation present in the restored wetland apparently had little or no effect. The removals are in good agreement with those observed by Gross et al. (2004) for ibuprofen in a wetland-river system (47 ± 37%) and the almost no attenuation found for ibuprofen (0%), naproxen (1%) and caffeine (0%) in a forest wetland-river system (Conkle et al., 2008). From the flow rates of the two rivers, the concentration of the studied compounds shown in Table 1, and the removal efficiencies calculated in this section, it was estimated that the restored wetland would enable the removal of 7 kg per month of these contaminants from the Aarhus river.

4. Conclusions

Emerging contaminants, including pesticides, PCPs, pharmaceuticals, plasticizers and fire retardants, occur in varying concentrations in rivers and lakes in the agricultural area of North-East Denmark. Seventeen emerging contaminants were identified and quantified in the surface waters with concentrations ranging between 2 and 1476 ng L^{-1}. Diclofenac, MCPA, caffeine, and TCEP were the most abundant, and MCPA was the compound most commonly detected at all sampling sites. The outlet channel from the river-lake system contained the highest number and the highest concentrations of emerging contaminants probably because of discharge of combined sewer overflows and effluents from WWTPs. The rivers that drained intensive agricultural areas and also received effluents from WWTPs upstream in the catchments also contained high concentrations of emerging contaminants, particularly pesticides after heavy rain episodes, whereas the abundance of pharmaceuticals and PCPs was rather conservative. The restored wetland, which had a relatively short water retention time, were able to attenuate some of the emerging pollutants The attenuation efficiency of the emerging contaminants was compound dependent and ranged from no attenuation to 84%. Although the study indicates that the restored wetland may play a significant role in the attenuation of selected emerging contaminants, further work is needed to confirm these observations. Reducing the abundance of emerging contaminants should be considered a priority in order to restore the good chemical and ecological status of natural surface waters.

Acknowledgments

This study was financed by the Spanish Ministry of Science and Innovation, Project CTM2008-0647-C02-02/TECNO and the Danish Council for Independent Research – Natural Sciences, Project 10-083195. Dr. VM received a Juan de la Cierva contract from the Spanish Ministry of Science and Innovation.

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