NEW PHARMACEUTICALS AND THEIR TRANSFORMATION PRODUCTS IN DRINKING AND SURFACE WATERS OF KARACHI (PAKISTAN)

Scheurell M[1], Hühnerfuss H[1]*, Selke S[1,2], Shah MR[3]

[1]Institute of Organic Chemistry, University of Hamburg, Martin-Luther-King-Pl. 6, 20146 Hamburg, Germany
[2]Eurofins GfA Lab Service GmbH, Neuländer Kamp 1, 21079 Hamburg, Germany
[3]HEJ Research Institute of Chemistry, University of Karachi, Karachi, Pakistan

Introduction

Pharmaceuticals and personal care products (PPCPs) have been detected in many environmental samples taken in highly industrialized countries in wastewater and surface waters, and they are thus classified as emerging pollutants[1-4]. However, at the beginning of the present study, it was generally assumed that in developing countries the "classical" pesticides of the first and second generation are prevailing in all environmental compartments. Our first results of this endeavour showed that this assumption has to be modified considerably[5]. Extremely high concentrations of pharmaceuticals were encountered in the present Pakistanian water samples while the classical pesticides did not play a major role. These high concentrations allowed a detailed investigation of "new" environmental pharmaceuticals as well as of the formation of new transformation products.

Materials and methods

In Karachi, Pakistan, surface water samples were collected during two campaigns in December 2006 and April 2007 (Fig. 1). Sample 1 was taken from the Malir River, while samples 7 and 9 stem from the Lyari River, the two major rivers flowing through Karachi. Sample 3 was taken in the mangrove lagoon, which is part of Karachi harbor receiving effluents from the center parts of the city. Samples 4, 5, 6 and 8 were taken from an open drainage canal system (Korangi drain) receiving untreated residential and industrial effluents as well as wash-off and rain water from the Landhi residential district. Sample 2 was taken from the end of a pipe eluting waste waters from the district of Clifton across the beach into the Arabian Sea.

All samples were taken in 2.5 L amber glass bottles with a sampling device designed in the working group and filtered through a glass fibre filter (GF-A, Whatman), a sample volume of 2 L of which was extracted over 1 g of Oasis HLB (Waters, Germany). After extraction of the sample the solid phase was dried with nitrogen, before being eluted with 40 mL of methanol. The resulting methanol eluates were then evaporated to dryness and derivatized with methyl chloromethanoate (MCM), according to ref[10], to form the methyl esters (COOH-functions) or carbonate diesters (HO-functions), respectively. The resulting *n*-hexane phase of the derivatization reaction was spiked with 100 µL of an internal standard (mecoprop methyl ester [1 µg/mL]) and evaporated under a gentle stream of nitrogen to a final volume of 100 µL. GC-MS analysis was performed on a Magnum ITD 40 (Finnigan MAT, Bremen, Germany) ion trap mass spectrometer with the following conditions: EI at 70 eV, manifold temperature 473 K, emission current 10 µA, dwell time 100 µs, and scan range 40-500 m/z (full scan mode). It was coupled to a Varian 3400 GC system (Sunnyvale, CA, USA), separation was performed on a VF-5MS column, analogue to DB-5 (Varian, Sunnyvale, CA, USA), length 30 m, ID 0.2 mm, film thickness 0.33 µm, carrier gas Helium 5.0, transfer line 523 K run with an A 200 SE autosampler (CTC Analytics, Zwingen, Switzerland), injected volume 2 µL. The column was temperature programmed as follows: 333 K (2.5 min) with 6 K/min to 523 K (kept for 15 min).

Results and discussion:

In the present investigation an integrative approach was followed combining chemical-analytical and ecotoxicological aspects. 768 fractions from 32 samples were screened for their ecotoxicological relevance by the luminescent bacteria test. The samples originate from all parts of the drinking water circuit, including the sources (ground water and surface water), distribution, processing and tapping points as well as waste water. The determined pollution status indicates the alarming condition of the drinking water circuit. However, contrary to our expectation, not the "classical" pesticides of the first and second generation were prevailing. The waste and surface waters of the city area of Karachi were severely contaminated with PPCPs and industrial chemicals. The latter results were already published in an earlier paper[5].

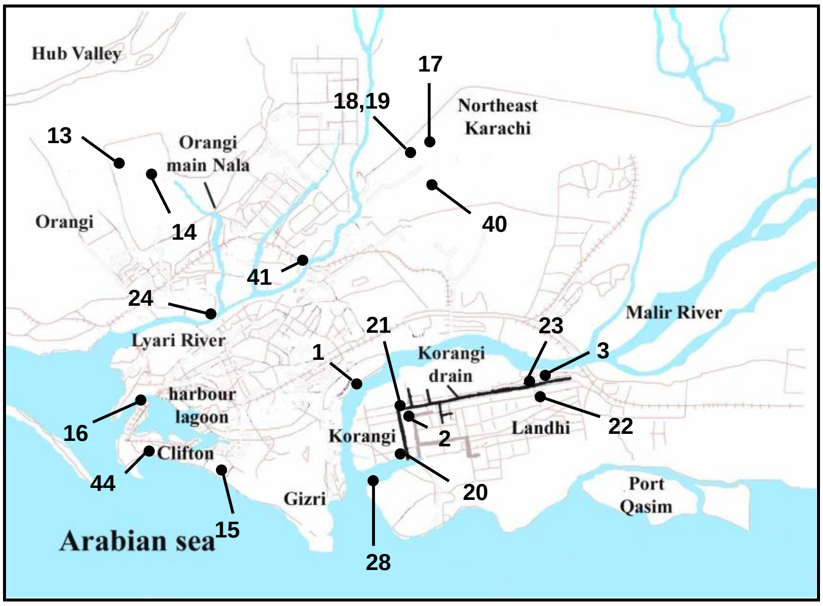

Fig. 1: Map of Karachi showing the rivers and the draining system, sampling locations are marked (●)

The high concentrations of the parent compounds and their transformation products allowed the determination of the molecular structure of several "new" environmental contaminants as well as environmental metabolites detected in drinking and surface waters for the first time. Examples for this part of our investigation are summarized in Tables 1 and 2. In the first column of these Tables the respective molecular structures are shown, in the second column the names, concentration ranges as well as the "novelty" of their appearance in environmental water samples are given, while in the third column the mass spectra as obtained from the sample extracts are displayed. In all cases the reference spectra measured from compounds commercially available or synthesized in our lab were identical (not shown herein).

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References:

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4. Khetan SK, T.J. Collins TJ (2007), *Chem Rev* 107: 2319
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6. Andreozzi R, Raffaele M, Nicklas P (2003), *Chemosphere* 50: 131^9

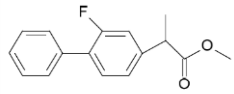
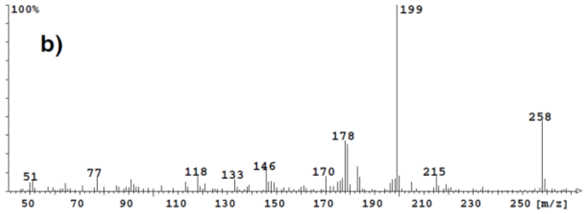
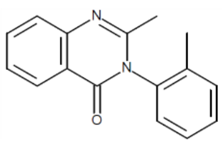
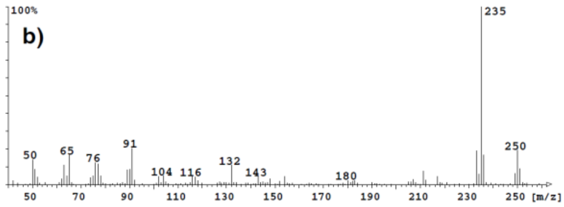
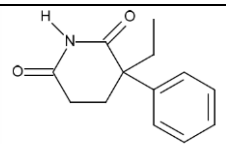
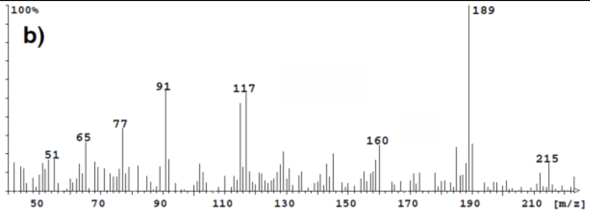
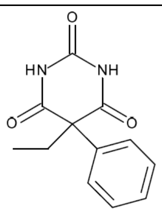
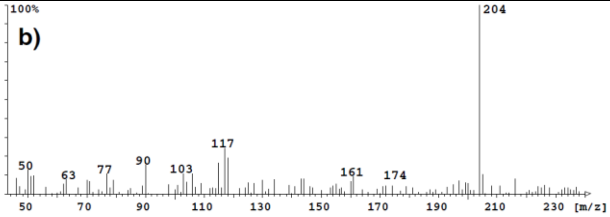
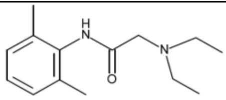
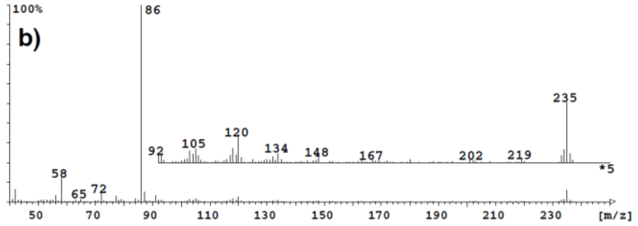
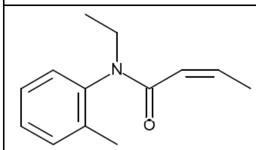
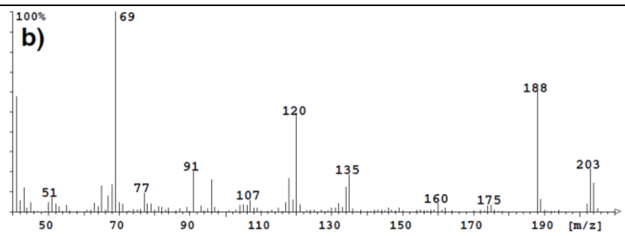
Molecular Structure	Name	Mass Spectrum
	Fluorbiprofen (Stat. 1) Thus far in two WWT plants only [6]; In Karachi found in all surface water samples between 40 – 470 ng/L, in drinking water 1 – 70 ng/L	
	Methaqualon (Stat 21) Substitute of barbiturates; Produced illegally; In Karachi in four waste water samples between 2– 900 ng/L; in sea water sample (Gizri Bight) 190 ng/L	
	Glutethimid (Stat. 20) Substitute of barbiturates; In Karachi in two waste water samples and three surface water samples between 7 – 65 ng/L	
	Phenobarbitol (Stat 20) Sedativum/anticonvulsivum; Thus far in some WWT plants in the USA and Europe, factory area in Berlin; In Karachi in two waste water samples, in Gizri Bight between 20 – 90 ng/L and in one drinking water sample 1 ng/L	
	Lidocain (Stat. 20) Local anaesteticum, also in connection with cocain;; thus far in WWT and surface water samples in the EU; In Karachi ubiquitously in all water samples between 5 and 1900 ng/L; in one drinking water sample 2 ng/L.	
	Crotamiton (Stat. 20); Against itch mites; Thus far in Europe in some WWT and surface water samples; in Japan ubiquitously; In Karachi in seven waste water and surface water samples between 5 – 160 ng/L; In two River Indus samples 1 ng/L:	

Table 1: Examples for PPCPs in surface and drinking water of Karachi (Pakistan) thus far not or seldom found in environmental samples

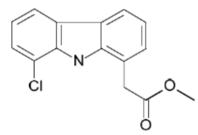
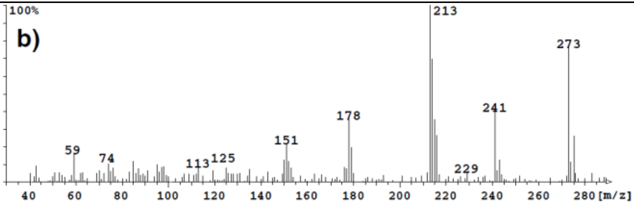
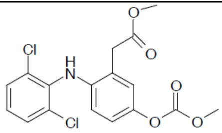
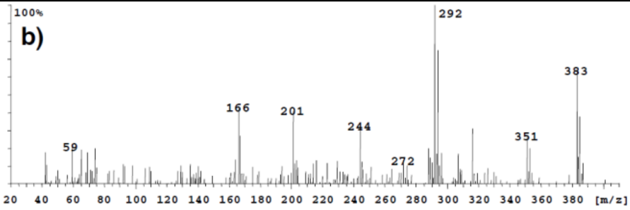
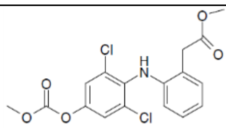
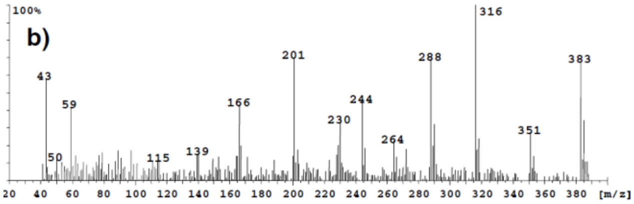
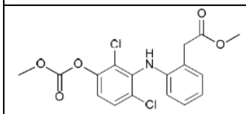
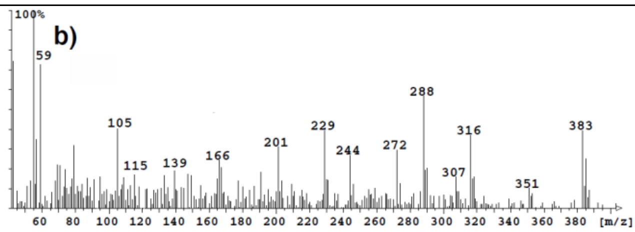
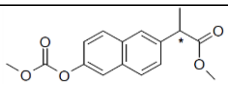
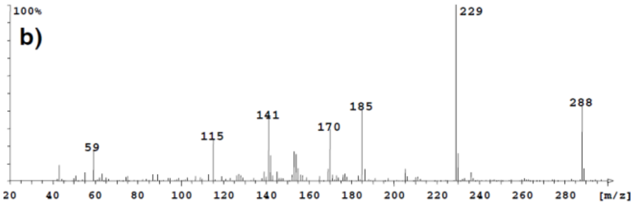
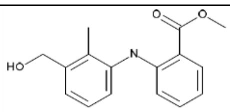
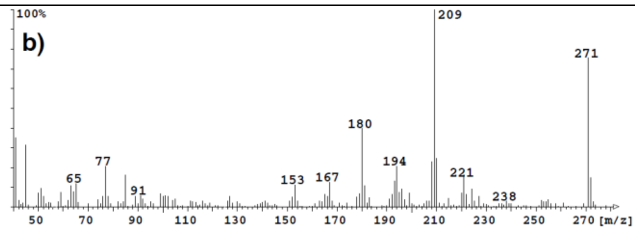
Molecular Structure	Name	Mass Spectrum
	**8-Chlorcarbazol-1-yl-ethansäure**, MCM-Derivate (Stat. 1) Phototransformationprod. of Diclofenac; "new" in environm. samples; In Karachi in three surface and three waste water samples between 35 – 370 ng/L	
	**5-Hydroxy-diclofenac**, MCM-Derivate (Stat. 15) Phototransformationprod. of Diclofenac; "new" in environm. samples; in Karachi in waste water 140 – 300ng/L: in the Malir River 80 ng/L; in the Lyari River 15 ng/L	
	**4'-Hydroxy-diclofenac**; MCM-Derivate (Stat. 15) Phototransformationprod. of Diclofenac;"new" in environm. samples; in waste water between 580 – 1800 ng/L; in both rivers between 420 and 780 ng/L	
	**3'-Hydroxy-diclofenac** MCM-Derivate (Stat. 15) Phototransformationprod. of Diclofenac;"new" in environm. samples; in three surface and five waste water samples between 85 – 300 ng/L	
	**6-*O*-Desmethylnaproxen**; MCM-Derivate (Stat. 15); "new" in waste water (also in Hamburg samples); in Karachi in waste water between 80 – 1100 ng/L; in surface w. 40-1400 ng/L	
	**3-hydroxy-mefenaminic acid** MCM-Derivate (Stat. 1) "new" in environm. samples; in Karachi in surface water between 2800–20500 ng/L; in waste water between 180 – 7700 ng/L	

Table 2: Examples for "new" transformation products of PPCPs found in water samples of Karachi (Pakistan)