Betablockers in Municipal Wastewaters in Switzerland

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INTRODUCTION

The ß-adrenergic blockers (betablockers) comprise a group of pharmaceuticals that are mostly used in the treatment of cardiovascular disorders such as hypertension, cardiac arrhythmia or ischemic heart disease.
After intake these drugs are excreted with urine either as the active substance or as metabolites. Human-use pharmaceuticals enter sewage effluents unchanged or metabolized via urine and feces and by improper disposal and eventually reach municipal wastewater treatment plants (WWTPs). However, direct inputs into ambient waters is also possible through storm water overflow and leaks in the sewer system.
To study the removal of selected betablockers, field studies were performed in a full-scale activated sludge treatment plant.

EXPERIMENTAL

Samples of 24-h flow proportional composites of primary (50 mL, inf) and tertiary effluents (150 mL, eff) were collected over 3 days.
Wastewater samples were enriched by solid-phase extraction, followed by reversed-phase liquid chromatography coupled to tandem mass spectrometry using positive electrospray ionization.
Atenolol-d7, sotalol-d6 and DL propranolol-d7 were used as surrogate standards.
Recoveries from treated wastewater were above 80% for atenolol, sotalol and propranolol.
Recoveries of metoprolol, that was quantified with the non-ideal standard propranolol-d7, were around 50%. The overall precision (n=6) ranged between 2 and 13%.The limit of quantification varied between 10 and 20 ng/L.

RESULTS + DISCUSSION

First results indicate that elimination in wastewater treatment plants is incomplete, and therefore residual amounts are discharged to ambient waters.
The removal from the wastewater stream during wastewater treatment was 74-82% for atenolol, 32-36 % for sotalol, 31-43% for metoprolol and 26-33% for propranolol.
This raises the question of what potential ecotoxicological impact betablockers have in natural waters at environmental concentrations.

In order to predict the environmental concentrations (PEC) in raw sewage the formula shown on the right can be used (A Joss, EAWAG, personal communication).The calculation assumes that the estimated consumption is evenly distributed over the year and throughout the geographic area and that no biodegradation is assumed in the sewer before the WWTP. The human metabolism was considered and a urine production of 1.25 L per person and day was assumed. The predicted (PEC) and measured (MEC) concentrations in raw sewage give comparable results, particularly for atenolol and sotalol.

ACKNOWLEDGEMENTS

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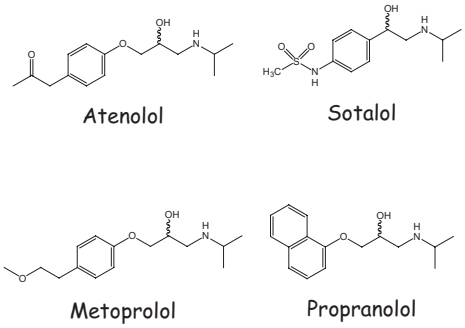
Betablockers



Analytical Method

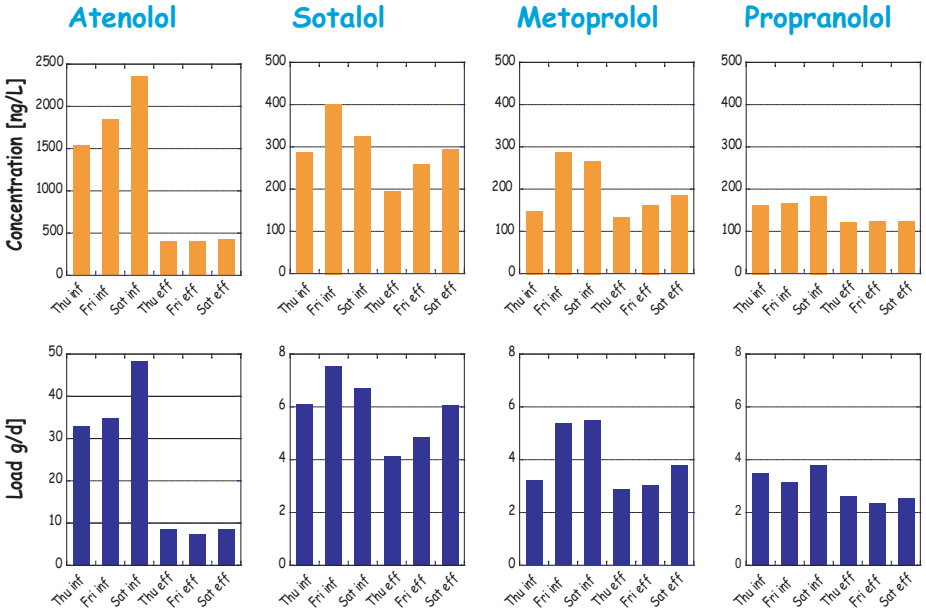
Filtration (glass fiber GF8)
pH adjustment to pH 6.5
Addition of deuterated surrogate standards

Enrichment on polymeric material (OASIS MCX)
Drying of cartridges with N_2
Elution with MeOH/1% NH_3
Evaporation to dryness with N_2
Reconstitution in H_2O/ACN

Separation on a C18 column

Detection with MS/MS (MRM)

Concentrations and Loads in a WWTP



Comparison of PECs and MECs in Raw Wastewater

	Excretion in urine unchanged (literature)	Swiss consumption [2004]* [kg/y]	PEC raw wastewater [ng/L]	MEC raw wastewater [ng/L]
Atenolol	90%	3'200	1'650	1540- 2350
Sotalol	70%	800	340	290- 400
Metoprolol	3-10%	3'200	190	150- 290
Propranolol	20%	800	90	160- 180

$$PEC_{raw}: \quad \frac{(C * 10^{12} * E / (365 * P) * (1 - SIWW)}{(AWW * 1000)}$$

$C * 10^{12}$: Consumption per year [ng/y]
E: Share of excretion in urine
P: Swiss Population (7'000'000)
SIWW: share of the industrial WW in the municipal WW (0.4)
AWW: Amount of Waste Water per capita and day (0.4 m^3 PE^{-1} d^{-1})