The fate of estrogens in a municipal sewage treatment plant


HENRIK ANDERSEN,1 HANSRUEDI SIEGRIST,2 BENT HALLING-SØRENSEN,1 AND THOMAS A. TERNES3*

1: The Danish University of Pharmaceutical Sciences, Institute of Analytical Chemistry, Universitetsparken 2, DK-2100 Copenhagen, Denmark
2: EAWAG, Ueberlandstrasse 133, 8600 Duebendorf, Switzerland
3: Bundesanstalt für Gewässerkunde (BfG), Kaiserin-Augusta-Anlagen 15-17, D-56068 Koblenz, Germany

Abstract

The fate of the highly potent endocrine disrupters estrone (E1), 17β-estradiol (E2) and 17α-ethinylestradiol (EE2) was investigated in mechanical and biological sewage treatment as well as in sewage-sludge treatment at a municipal German sewage treatment plant (STP). The main outcome of the study was that a common municipal STP with an activated sludge system for nitrification and denitrification including sludge recirculation can appreciably eliminate natural and synthetic estrogens. As a consequence, the endocrine effects of biota in the receiving waters should be significantly reduced. All estrogen concentrations decreased gradually along the treatment train. In the STP effluent, the steroid estrogen concentrations were always below the quantification limit of 1 ng/L. The elimination efficiency of the natural estrogens (E1 and E2) exceeded 98% and EE2 was reduced by more than 90%. The natural estrogens were largely degraded biologically in the denitrifying and aerated nitrifying tanks of the activated sludge system, whereas EE2 was only degraded in the nitrifying tank. Only about 5% of the estrogens are sorbed onto digested sewage sludge. It is very likely that conjugates (glucuronides and sulfates) of the estrogens were cleaved into the parent compounds mainly in the first denitrification tank.
Analysis of acidic pharmaceuticals, antibiotics and ivermectin in river sediment using LC-tandem MS


Dirk Löffler, Thomas A. Ternes

German Federal Institute of Hydrology, P.O. Box 20 02 53, D-56002 Koblenz

Abstract
Analytical methods have been developed for the determination of 8 acidic pharmaceuticals and 2 metabolites, 7 antibiotics and the antiparasitic ivermectin in river sediment. The sediments were solvent extracted with ultrasonic assistance. A solid phase extraction (SPE) clean-up step was performed thereafter. The acidic compounds clofibric acid, diclofenac, fenoprofen, gemfibrozil, ibuprofen, 2-hydroxy-ibuprofen, indomethacin, ketoprofen, naproxen and the antiparasitic ivermectin were measured in the negative mode by LC-APCI-tandem MS, whereas the antibiotics clarithromycin, erythromycin, roxithromycin, sulfadiazine, sulfamethazine, sulfamethoxazole and trimethoprim were detected in the positive mode by LC-ESI-tandem MS. Bezafibrate could not be determined using the method developed. The limit of quantification (LOQ) ranged from 0.4 to 8 ng·g⁻¹ for the acidic pharmaceuticals, sulfadiazine and ivermectin and was 20 ng·g⁻¹ for the other antibiotics.
Ozonation: A tool for removal of pharmaceuticals, contrast media and musk fragrances from wastewater?


THOMAS A. TERNES, JEANNETTE STÜBER, NADINE HERRMANN, DEREK MCDOWELL, ACHIM RIED, MARTIN KAMPMANN, BERNHARD TEISER

1: ESWE-Institute for Water Research and Water Technology, D-65201 Wiesbaden, Söhnleinstrasse 158, Germany
2: Wedeco, Boschstraße 6, 32051 Herford, Germany
3: Abwasserverband Braunschweig, Celler Heerstraße 337, D-38112 Braunschweig, Germany

Abstract

A pilot plant for ozonation and UV-disinfection received effluent from a German municipal sewage treatment plant (STP) to test the removal of pharmaceuticals, iodinated X-ray contrast media (ICM) and musk fragrances from municipal wastewater. In the original STP effluent, 5 antibiotics (0.34-0.63 µg l⁻¹), 5 betablockers (0.18-1.7 µg l⁻¹), 4 antiphlogistics (0.10-1.3 µg l⁻¹), 2 lipid regulator metabolites (0.12-0.13 µg l⁻¹), the antiepileptic drug carbamazepine (2.1 µg l⁻¹), 4 ICM (1.1-5.2 µg l⁻¹), the natural estrogen estrone (0.015 µg l⁻¹) and 2 musk fragrances (0.1-0.73 µg l⁻¹) were detected by LC-electrospray tandem MS and/or GC/MS/MS. ICM, derived from radiological examinations, were present with the highest concentrations (diatrizoate: 5.7 µg l⁻¹, iopromide: 5.2 µg l⁻¹). By applying 10-15 mg l⁻¹ ozone (contact time: 18 min), all the pharmaceuticals investigated as well as musk fragrances (HHCB, AHTN) and estrone were no longer detected. However, ICM (diatrizoate, iopamidol, iopromide and iomeprol) were still detected in appreciable concentrations. Even with a 15 mg l⁻¹ ozone dose, the ionic diatrizoate only exhibited removal efficiencies of no higher than 14 %, while the non-ionic ICM were removed to a degree of higher than 80 %. Advanced oxidation processes (O₃/UV-low pressure mercury arc, O₃/H₂O₂), which were non-optimized for wastewater treatment, did not lead significantly to a higher removal efficiency for the ICM than ozone alone.
Analytical method for the determination of the aminoglycoside gentamicin in hospital wastewater via LC-electrospray-tandem MS

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Dirk Löffler, Thomas A. Ternes

ESWE-Institute for Water Research and Water Technology, Soehnleinstrasse 158, D-65201 Wiesbaden

**Abstract**

A method for the determination of gentamicin residues in hospital wastewater has been developed using kanamycin as a surrogate standard. The method consists of solid phase extraction (SPE) and detection by ion-pair chromatography with electrospray tandem mass spectrometry (LC-ES tandem MS). The SPE was performed on a weak cation exchanger. Filtration should be avoided in the sample preparation, otherwise a significant loss of gentamicin occurs. Chromatographic separation on a C₁₈-column was achieved using a ternary eluent containing methanol, water and 20 mmol l⁻¹ heptafluorobutyric acid solution. Mean relative recoveries of the analytes in hospital wastewater varied between 107 % and 111 %. The limit of quantification (LOQ) was 0.20 µg l⁻¹ in hospital wastewater. Gentamicin was found in native hospital wastewater in a concentration range between 0.4 -7.6 µg l⁻¹.
Determination of estrogens in sludge and sediments by liquid extraction and GC/MS/MS

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Thomas A. Ternes¹, Henrik Andersen², Daniel Gilberg³, Matthias Bonerz¹

¹: ESWE-Institute for Water Research and Water Technology, D-65201 Wiesbaden, Soehnleinstraße 158, Germany
²: The Royal Danish School of Pharmacy, Institute of Analytical and Pharmaceutical Chemistry. Section for Environmental Chemistry. Universitetsparken 2, DK-2100 Copenhagen, Denmark
³: Ecotoxicology GmbH, Böttgerstraße. 2-14, D-60437 Flörsheim am Main, Germany

Abstract

Two methods have been developed which enable the determination of estrogens in digested and activated sludge from domestic sewage treatment plants (STPs) down to 2 ng/g and in freshwater sediments down to 0.2 ng/g. The method for sludge analysis consists of solvent extraction, a gel permeation chromatography (GPC) clean-up step 1 g silica gel column and finally detection by GC-ion trap MS/MS of the silylated estrogens with MSTFA. For sediments the solvent extraction was successively followed by silica gel clean up, solid phase enrichment (SPE) and a HPLC clean up before derivatization and GC/MS/MS detection. Mean recoveries of the estrogens mainly exceeded 70 % in sludge and 90 % in sediments. In activated and digested sewage sludge, estrone and 17β-estradiol were detected up to 37 ng/g and 49 ng/g, respectively, and 17α-ethinylestradiol up to 17 ng/g. The occurrence of estrogens in digested sludge indicates that estrogens can be persistent during sludge digestion. In activated and digested sewage sludge, estrone and 17β-estradiol were detected up to 2 ng/g (estrone) and the contraceptive 17α-ethinylestradiol was found with a maximum of 0.9 ng/g. Mestranol, a prodrug for 17α-ethinylestradiol, was not detected in either sludge or in sediments.
Removal of Pharmaceuticals during drinking water treatment


Thomas A. Ternes¹*, Martin Meisenheimer¹, Derek McDowell¹, Frank Sacher², Heinz-Jürgen Brauch², Brigitte Haist-Gulde², Gudrun Preuss³, Uwe Wilme³, Ninette Zulei-Seibert³

¹: ESWE-Institute for Water Research and Water Technology, D-65201 Wiesbaden, Söhnelinstasse 158, Germany
²: DVGW-Technologiezentrum Wasser, Karlsruher Str. 84, D-76139 Karlsruhe, Germany
³: Institute for Water Research GmbH, Zum Kellerbach 46, D-58239 Schwerte, Germany

Abstract

The elimination of selected pharmaceuticals (bezafibrate, clofibric acid, carbamazepine, diclofenac) during drinking water treatment processes was investigated at lab and pilot scale, and in real waterworks. No significant removal of pharmaceuticals was observed in batch experiments with sand under natural aerobic and anoxic conditions, thus indicating low sorption properties and high persistence with non-adapted microorganisms. These results were underscored by the presence of carbamazepine in bank filtrated water with anoxic conditions in a waterworks area. Flocculation using Fe(III)chloride in lab-scale experiments (Jar test) and investigations in waterworks exhibited no significant elimination of the selected target pharmaceuticals. However, ozonation was in some cases very effective in eliminating these polar compounds. In lab-scale experiments, 0.5 mg/L ozone has shown to reduce the concentrations of diclofenac and carbamazepine by more than 90 %, while bezafibrate was eliminated by 50 % with a 1.5 mg/L ozone dose. Clofibric acid was stable even at 3 mg/L of ozone. Under waterworks conditions, similar removal efficiencies were observed. In addition to ozonation, filtration with granular activated carbon (GAC) was very effective in removing pharmaceuticals. Except for clofibric acid, GAC in pilot scale experiments and waterworks provided a major elimination of the pharmaceuticals under investigation.