PHARMACEUTICAL ABSTRACTS RISK TO ECOSYSTEM, REMOVAL WITH WATER & SEWAGE TREATMENT

Prepared by:

December 2005

#200-661 East Burnside Road, Victoria, British Columbia

Tel 250.360-1398 Fax 250.381.3521 www.BuckSuzuki.org

TABLE OF CONTENTS

THE CONCERN

Most pharmaceuticals are metabolized only incompletely by patients and enter the municipal sewage with the patients' excretions. Some municipal sewage systems send these pharmaceuticals freely into the planets ecosystem. Some pharmaceuticals such as anti-tumour agents are carcinogenic, mutagenic, teratogenic and fetotoxic. Some pharmaceuticals and personal care products of concern, including painkillers (aspirin, ibuprofen), cholesterol control medication (clofibric acid, bezafibrate), antibacterial agents (triclosan), musks (including galaxolide and tonalide), X-ray contrast media (diatrizoate), cancer treatment drugs (cyclophosphamide), anti-seizure medication (carbamazepine), nonsteroidal anti-inflammatory drugs (diclofenac) and anti-depressant drugs (fluvoxamine) are investigated below.

PHARMACEUTICAL AND PERSONAL CARE PRODUCTS IN SEWAGE TREATMENT WORKS

Rakesh Kanda, Paul Griffin, Huw A. James and James Fothergill *Journal of Environmental Monitoring*, 2003, 5(5), 823 - 830
DOI: 10.1039/b306355k

In this study a number of analytical procedures are described to determine pharmaceuticals and personal care products (PPCPs) and their metabolites during sewage treatment. The work shows that PPCPs occur in sewage influent and are removed by various wastewater treatment processes. PPCPs include a wide range of chemicals such as prescription drugs as well as diagnostic agents, fragrances, sun-screen agents, and various other compounds commonly present in household items (*e.g.* detergents, cleaners, toothpastes *etc.*). During this study a number of PPCPs including painkillers (aspirin, ibuprofen), cholesterol control medication (clofibric acid), antibacterial agents (triclosan), musks (including galaxolide and tonalide), X-ray contrast media (diatrizoate), cancer treatment drugs (cyclophosphamide) and anti-depressant drugs (fluvoxamine) were investigated. Analysis was carried out using a number of techniques. Samples were extracted using solid phase extraction or liquid-liquid extraction and the extracts analysed using capillary gas chromatography-mass spectrometry (GC-MS) with selected ion monitoring or liquid chromatography mass spectrometry (LC-MS) or LC-MS-MS. The results obtained show that aspirin, clofibric acid, diatrozate, fluvoxamine and cyclophosphamide were not detected in any of the crude sewage or sewage effluent samples above the limit of detection of the applied methods. Ibuprofen was detected in all crude sewage samples as well as in all effluent samples with one exception. Removal of ibuprofen by the different STWs was generally between 80–100%, with the exception of one STW where removal was poor (14.4 to 44%). Triclosan was also detected in all crude sewage samples and in all sewage effluent samples. The highest concentration of triclosan detected was 3100 ng l^{-1}. A high removal efficiency was observed in effluent samples taken on two occasions (average removal 95.6%). The concentrations of musks detected in the crude sewage were generally low except for galaxolide and tonalide. The results from STW effluent samples showed significant removal of galaxolide (70–83% removal) except at one STW (STW 1) where removal was low (57% and 39%). Similar removal efficiencies for tonalide were achieved at these STWs (73–96%) except at STW 1 where removal was poor (53%).

BIODEGRADABILITY OF CEFOTIAM, CIPROFLOXACIN, MEROPENEM, PENICILLIN G, AND SULFAMETHOXAZOLE AND INHIBITION OF WASTE WATER BACTERIA

A. Al-Ahmad [A1], F. D. Daschner [A1], K. Kümmerer [A1]

[A1] Institute of Environmental Medicine and Hospital Epidemiology, Hugstetterstraße 55, D-79106 Freiburg, Germany

Archives of Environmental Contamination and Toxicology Publisher: Springer-Verlag New York ISSN: 0090-4341 (Paper) 1432-0703 (Online) DOI: 10.1007/s002449900501 Issue: Volume 37, Number 2 Date: August 1999 Pages: 158 - 163

Abstract. Most antibiotics are metabolized only incompletely by patients after administration and enter the municipal sewage with the patients' excretions. Little is known about their biodegradability in aquatic environments and their role with respect to growing bacterial resistance. Therefore, the biodegradability of some clinically important antibiotic drugs as a very first step of an environmental risk assessment was investigated with the OECD closed bottle test (CBT). To assess toxicity of the test compounds against aquatic bacteria (1) a growth inhibition test (GIT) with Pseudomonas putida was conducted; (2) a toxicity control was used in the CBT; and (3) the colony-forming units (CFUs) were monitored in the test vessels. Theoretical concentrations of the test substances in hospital effluents were calculated and compared with minimum inhibitory concentrations for susceptible pathogenic bacteria. None of the test compounds met the criteria for ready biodegradability. Only penicillin G was biodegradable to some degree (27%), even when the test was prolonged from 28 to 40 days (35%). The inhibition concentrations measured in the GIT were in the same range or lower than the 50% minimum inhibitory concentrations (MIC50) known for susceptible pathogenic bacteria. CFU monitoring revealed high toxicity for sulfamethoxazole, whereas ciprofloxacin had a weak but significant effect; only for meropenem a weak but significant effect was measured in the toxicity control of the CBT. MIC50 published for susceptible pathogenic bacteria were for all compounds in the same range as the concentrations expected for hospital effluents. Therefore, antibiotic drugs emitted into municipal sewage may affect the biological process.

BIODEGRADABILITY OF THE ANTI-TUMOUR AGENT IFOSFAMIDE AND ITS OCCURRENCE IN HOSPITAL EFFLUENTS AND COMMUNAL SEWAGE

Kuemmerer, Klaus; Steger-Hartmann, Thomas; Meyer, Michael
WATER RES. Vol. 31, no. 11, pp. 2705-2710. Nov 1997.

A portion of administered pharmaceuticals are excreted unmetabolised by patients and can be found in hospital effluent and municipal sewage. Some pharmaceuticals such as anti-tumour agents are carcinogenic, mutagenic, teratogenic and fetotoxic. Little is known about their environmental impact. Therefore, the biodegradability of the widely used anti-tumour agent ifosfamide (IF) was assessed with the modified Zahn-Wellens test (OECD 302 B) and a test simulating biological sewage treatment. The biodegradation was monitored by DOC and GC/MS. The concentration of IF in hospital effluent, communal sewage and the effluent from a communal sewage treatment plant (STP) was analyzed as well as calculated by the amounts of water and IF used in hospitals. The expected concentration of IF in German surface waters was calculated. IF was not biodegradable in the Zahn-Wellens test and the STP simulation test. It was not adsorbed by the sewage sludge. The concentrations measured in the hospital effluents, the STP influent and the STP effluent were of the same order of magnitude as the calculated ones, indicating that no adsorption, biodegradation or other elimination of IF took place to any noticeable extent.

REMOVAL OF PHARMACEUTICALS DURING DRINKING WATER TREATMENT.

Ternes TA, **Meisenheimer M**, **McDowell D**, **Sacher F**, **Brauch HJ**, **Haist-Gulde B**, **Preuss G**, **Wilme U**, **Zulei-Seibert N**. Environ Sci Technol. 2002 Sep 1;36(17):3855-63.

ESWE-Institute for Water Research and Water Technology, Wiesbaden, Germany. Thomas.ternes@ESWE.com

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 nonadapted microorganisms. These results were underscored by the presence of carbamazepine in bank-filtrated water with anaerobic conditions in a waterworks area. Flocculation using iron(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 was 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 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.

FROM MUNICIPAL SEWAGE TO DRINKING WATER: FATE AND REMOVAL OF PHARMACEUTICAL RESIDUES IN THE AQUATIC ENVIRONMENT IN URBAN AREAS.

Heberer T, Reddersen K, Mechlinski A. Water Sci Technol. 2002;46(3):81-8.

Institute of Food Chemistry, Technical University of Berlin, Germany.

Recently, the occurrence and fate of pharmaceutically active compounds (PhACs) in the aquatic environment was recognized as one of the emerging issues in environmental chemistry and as a matter of public concern. Residues of PhACs have been found as contaminants in sewage, surface, and ground- and drinking water samples. Since June 2000, a new long-term monitoring program of sewage, surface, ground- and drinking water has been carried out in Berlin, Germany. Samples, collected periodically from selected sites in

the Berlin area, are investigated for residues of PhACs and related contaminants. The purpose of this monitoring is to investigate these compounds over a long time period to get more reliable data on their occurrence and fate in the different aquatic compartments. Moreover, the surface water investigations allow the calculation of season-dependent contaminant loads in the Berlin waters. In the course of the monitoring program, PhACs and some other polar compounds were detected at concentrations up to the microg/L-level in all compartments of the Berlin water cycle. The monitoring is accompanied and supported by several other investigations such as laboratory column experiments and studies on bank filtration and drinking water treatment using conventional or membrane filtration techniques.

DETERMINATION OF POLAR PHARMACEUTICALS IN SEWAGE WATER OF GREECE BY GAS CHROMATOGRAPHY-MASS SPECTROMETRY.

Koutsouba V, Heberer T, Fuhrmann B, Schmidt-Baumler K, Tsipi D, Hiskia A.

General Chemical State Laboratory, Pesticide Residues Laboratory, An. Tsoha 16, 11521 Athens, Greece.

Sewage influents and effluents of different urban areas of Greece, were analyzed for polar pharmaceutical residues, used in human medicine. Drugs investigated were the anti-inflammatory drugs diclofenac and ibuprofen, the metabolite of the drugs clofibrates used as blood lipid regulators, clofibric acid and the analgesics phenazone and propyphenazone. Analysis was carried out using capillary gas chromatography-mass spectrometry with selected ion monitoring. The method used was involved solid phase extraction (C(18)) and derivatization with pentafluorobenzyl bromide. Diclofenac was detected in every sewage effluent sample.

ACIDIC PHARMACEUTICALS IN SEWAGE-METHODOLOGY, STABILITY TEST, OCCURRENCE, AND REMOVAL FROM ONTARIO SAMPLES.

Lee, H.-B.; Sarafin, K.; Peart, T.E.; Lewina Svoboda, M.
Water Quality Research Journal of Canada. Vol. 38, no. 4, pp. 667-682. 2003

A gas chromatography/mass spectrometry (GC/MS) method for the determination of 11 selected acidic pharmaceuticals in sewage influent and effluent at trace levels has been developed. The drugs studied were salicylic acid, clofibric acid, ibuprofen, acetaminophen, gemfibrozil, fenoprofen, naproxen, ketoprofen, diclofenac, fenofibrate, and indomethacin, which are commonly used as analgesic/anti-inflammatory agents or lipid regulators. The antibacterial agent triclosan was also included in this study. A solid-phase extraction procedure using the Waters Oasis HLB (hydrophilic-lipophilic balance) cartridge was optimized for the extraction and elution of these compounds. The acids were then converted into their trimethylsilyl (TMS) derivatives. Final analysis was performed with a

Mass Selective Detector in the EI/SIM (electron impact/selected ion monitoring) mode. Recoveries of the drugs in spiked distilled water samples at 1 and 0.1 mu g/L levels were better than 80%. Similar recoveries of the drugs were obtained from fortified final effluent samples except for acetaminophen, which could not be recovered even if the extraction was performed immediately. The detection limits for the drugs, based on a concentration factor of 1000, were between 10 and 20 ng/L. A stability study indicated that, except for salicylic acid and acetaminophen, the other acidic pharmaceuticals were better than 75% recovered after the samples had been stored at 4 degree C in the dark for up to seven days. This method has been applied to quantify acidic drugs in wastewater samples collected from several sewage treatment plants in Ontario. While clofibric acid, acetaminophen, fenoprofen, and fenofibrate have never been detected, the other eight compounds were found in nearly all the influent and effluent samples, from low mu g/L to low ng/L levels. Eight sewage treatment plants removed from 0 to 98% of these drugs from the influent.

OCCURRENCE OF NEUTRAL AND ACIDIC DRUGS IN THE EFFLUENTS OF CANADIAN SEWAGE TREATMENT PLANTS

Issn: 1552-8618
Journal: Environmental Toxicology and Chemistry
Volume: 22 Issue: 12 Pages: 2872-2880
Authors: Metcalfe, Chris D., Koenig, Brenda G., Bennie, Don T., Servos, Mark, Ternes, Thomas A., Hirsch, Roman
Article ID:10.1897/02-469

Abstract–Samples of influent (untreated) and effluent (treated) from 18 sewage treatment plants (STPs) in 14 municipalities in Canada were analyzed for residues of selected prescription and nonprescription drugs. Several neutral and acidic drugs were detected in effluents, including analgesic/anti-inflammatory agents, lipid regulators, and an antiepileptic drug, carbamazepine. Residues were extracted from effluents by solid-phase extraction, followed by either methylation and analysis of acidic drugs by gas chromatography/mass spectrometry or direct analysis of neutral drugs by liquid chromatography/tandem mass spectrometry. Analgesic/anti-inflammatory drugs such as ibuprofen and naproxen, as well as the metabolite of acetylsalicyclic acid, salicylic acid, were often detected in final effluents at μg/L concentrations. The acidic lipid regulator, clofibric acid, and the analgesic/anti-inflammatory drug diclofenac were not detected in any final effluent samples, which is not consistent with data from Europe. The precursor to clofibric acid, clofibrate, is not widely prescribed as a lipid regulator in Canada. However, the lipid regulators bezafibrate and gemfibrozil were detected in some samples of influent and effluent. The chemotherapy drugs ifosfamide and cyclophosphamide and the anti-inflammatory phenazone were not detected in influent or effluent samples, but the vasodilator drug pentoxyfylline was detected at ng/L concentrations in some final effluents. The widespread occurrence of carbamazepine at concentrations as high as 2.3 μg/L may be explained by use of this drug for other therapeutic purposes besides treatment of epilepsy and its resistance to elimination in STPs. The rates of elimination of ibuprofen and naproxen appeared to be elevated in STPs with hydraulic retention times for sewage greater than 12 h.

PHARMACEUTICALS AND PERSONAL CARE PRODUCTS IN THE ENVIRONMENT: AGENTS OF SUBTLE CHANGE?

Daughton CG, Ternes TA.

Environ Health Perspect. 1999 Dec;107 Suppl 6:907-38

Environmental Sciences Division, U.S. Environmental Protection Agency, ORD/NERL, Las Vegas, Nevada 89119, USA. daughton.christian@epa.gov

During the last three decades, the impact of chemical pollution has focused almost exclusively on the conventional "priority" pollutants, especially those acutely toxic/carcinogenic pesticides and industrial intermediates displaying persistence in the environment. This spectrum of chemicals, however, is only one piece of the larger puzzle in "holistic" risk assessment. Another diverse group of bioactive chemicals receiving comparatively little attention as potential environmental pollutants includes the pharmaceuticals and active ingredients in personal care products (in this review collectively termed PPCPs), both human and veterinary, including not just prescription drugs and biologics, but also diagnostic agents, "nutraceuticals," fragrances, sun-screen agents, and numerous others. These compounds and their bioactive metabolites can be continually introduced to the aquatic environment as complex mixtures via a number of routes but primarily by both untreated and treated sewage. Aquatic pollution is particularly troublesome because aquatic organisms are captive to continual life-cycle, multigenerational exposure. The possibility for continual but undetectable or unnoticed effects on aquatic organisms is particularly worrisome because effects could accumulate so slowly that major change goes undetected until the cumulative level of these effects finally cascades to irreversible change--change that would otherwise be attributed to natural adaptation or ecologic succession. As opposed to the conventional, persistent priority pollutants, PPCPs need not be persistent if they are continually introduced to surface waters, even at low parts-per-trillion/parts-per-billion concentrations (ng-microg/L). Even though some PPCPs are extremely persistent and introduced to the environment in very high quantities and perhaps have already gained ubiquity worldwide, others could act as if they were persistent, simply because their continual infusion into the aquatic environment serves to sustain perpetual life-cycle exposures for aquatic organisms. This review attempts to synthesize the literature on environmental origin, distribution/occurrence, and effects and to catalyze a more focused discussion in the environmental science community.

REMOVAL OF PHARMACEUTICAL RESIDUES AND OTHER PERSISTENT ORGANICS FROM MUNICIPAL SEWAGE AND SURFACE WATERS APPLYING MEMBRANE FILTRATION

Thomas Heberer Technical University of Berlin

Dirk Feldmann Central Institute of Bundeswehr Medical Service

Kirsten Reddersen Technical University of Berlin

Hans-Jürgen Altmann Bundeswehr Scientific Institute for Protection

Thomas Zimmermann Federal Ministry of Defense

ABSTRACT

In military out of area missions, it may be necessary to produce drinking water even from highly contaminated surface waters. These waters may contain a large number of organic, inorganic, and microbiological contaminants such as pharmaceutically active compounds (PhACs), pesticides, flame retardants, and heavy metals. The mobile drinking water purification units must be able to remove such contaminants as much as possible to meet the requirements of the maximum tolerance levels for drinking water set by the German and also by the European legislation. In the course of a research project, we investigate two drinking water purification units using the membrane filtration technique. Presently, these units undergo extensive long-term trials. If the testing of the new devices is positive regarding their functionality and their ability to remove all possible contaminants (also including radioactive compounds), they shall substitute the conventional devices using some chemicals and charcoal filtration for water purification. The new membrane purification units are much lower in costs and the drinking water that is generated has much higher acceptance regarding its organoleptic quality. In 2000, we tested a mobile drinking water purification unit, commercially available since 1999. This unit is able to generate up to 1600 liters of drinking water per hour. In a field study at the Teltowkanal, a canal carrying a high burden of municipal sewage effluents, the functionality and the efficiency of this device was tested to remove high amounts of algae, microbes, and organic and inorganic pollutants. The results from this fatigue test proved the ability of the water purification unit to reduce all contaminants to meet the maximum tolerance levels set by the drinking water regulation. Residues of PhACs have almost totally been removed from the surface water where these contaminants are found at individual concentrations up to the µg/L level. The prefiltration device was very effective in its ability to remove algae and solid particles, to protect the membranes from clogging, and to enable an almost maintenance-free operation. Some results from this study will be presented in this paper.

FACTORS AFFECTING THE CONCENTRATIONS OF PHARMACEUTICALS RELEASED TO THE AQUATIC ENVIRONMENT

David L. Sedlak University of California

Karen E. Pinkston University of California

http://www.ucowr.siu.edu/updates/pdfn/V120_A7.pdf

ABSTRACT

Although recent research has demonstrated that pharmaceuticals are widely distributed in the aquatic environment, it is difficult to assess the threat that they pose to drinking water supplies or their rate of attenuation in natural systems without an adequate understanding of the sources of contamination. To identify pharmaceutical compounds of significance to

water supplies in the United States, we have reviewed available data on the use of prescription drugs. Results of our analysis indicate that approximately 40 compounds could be present in municipal wastewater effluent at concentrations above 1,000 ng/L and at least 120 compounds could be present at concentrations above 1 ng/L. Important classes of prescription drugs include analgesics, beta-blockers, and antibiotics.

Analysis of a group of the most commonly used pharmaceuticals in the United States indicates that they are ubiquitous in wastewater effluents. We have detected concentrations ranging from approximately 10- 3,000 ng/L for high use pharmaceuticals such as betablockers (*e.g.,* metoprolol, propranolol) and acidic drugs (*e.g.,* gemfibrozil, ibuprofen). The concentration of pharmaceuticals in effluent from conventional wastewater treatment plants is similar. Advanced wastewater treatment plants equipped with reverse osmosis systems reduce concentrations of pharmaceuticals below detection limits. In addition to removal during biological wastewater treatment, pharmaceuticals also are attenuated in engineered natural systems (*i.e.,* treatment wetlands, ground water infiltration basins). Preliminary evidence suggests limited removal of pharmaceuticals in engineered treatment wetlands and nearly complete removal of pharmaceuticals during ground water infiltration.

PHARMACEUTICALS IN SURFACE WATERS

[Vorkommen von Pharmaka in Gewaessern]
Ternes, T.
Wasser und Boden. Vol. 53, no. 4, pp. 9-14. Apr. 2001

Out of 55 selected pharmaceuticals, 36 were found in the outflow from at least one German municipal sewage treatment plant. Maximum concentrations were detected with 6.3 mu g/l for the antiepileptic drug carbamazepine; maximum values of X-ray contrast agents were detected for iopamidol (15 mu g/l) and iopromide (11 mu g/l). In samples from 40 German rivers and streams, 31 pharmaceuticals and 5 metabolites were found in at least one sample. Median values in excess of 0.05 mu g/l were recorded for 6 pharmaceuticals and 4 X-ray contrast agents, as well the metabolites dehydrato-erythromycin and clofibric acid. The pharmaceutical contamination of the receiving waters is directly correlated to the proportion of treated and untreated municipal wastewater. Municipal wastewater consists mainly of domestic sewage, so that the detected pharmaceuticals stem mostly from use in human medicine and not from veterinary medicine. In addition to discharges from municipal sewage treatment plant, further point sources of contamination, especially for larger rivers such as Rhine and Main, can be expected to be industrial discharge outlets of pharmaceutical manufacturers.

BEHAVIOR OF PHARMACEUTICALS, COSMETICS AND HORMONES IN A SEWAGE TREATMENT PLANT.

Carballa M, Omil F, Lema JM, Llompart M, Garcia-Jares C, Rodriguez I, Gomez M, Ternes T. Water Res. 2004 Jul;38(12):2918-26.

Department of Chemical Engineering, School of Engineering, University of Santiago de Compostela, E-15782 Santiago de Compostela, Spain.

Two cosmetic ingredients (galaxolide, tonalide), eight pharmaceuticals (carbamazepine, diazepam, diclofenac, ibuprofen, naproxen, roxithromycin, sulfamethoxazole and iopromide) and three hormones (estrone, 17beta-estradiol and 17alpha-ethinylestradiol) have been surveyed along the different units of a municipal Sewage Treatment Plant (STP) in Galicia, NW Spain. Among all the substances considered, significant concentrations in the influent were only found for the two musks (galaxolide and tonalide), two anti-inflammatories (ibuprofen and naproxen), two natural estrogens (estrone, 17beta-estradiol), one antibiotic (sulfamethoxazole) and the X-ray contrast medium (iopromide), where the other compounds studied were below the limit of quantification. In the primary treatment, only the fragrances (30-50%) and 17beta-estradiol (20%) were partially removed. On the other hand, the aerobic treatment (activated sludges) caused an important reduction in all compounds detected, between 35% and 75%, with the exception of iopromide, which remained in the aqueous phase. The overall removal efficiencies within the STP ranged between 70-90% for the fragrances, 40-65% for the anti-inflammatories, around 65% for 17beta-estradiol and 60% for sulfamethoxazole. However, the concentration of estrone increased along the treatment due to the partial oxidation of 17beta-estradiol in the aeration tank.

ESTIMATION OF PHARMACEUTICAL RESIDUES IN PRIMARY AND SECONDARY SEWAGE SLUDGE BASED ON QUANTITIES OF USE AND FUGACITY MODELLING

Khan SJ, Ongerth JE.

School of Civil and Environmental Engineering, The University of New South Wales, Kensington, Australia. s.khan@unsw.edu.au **Water Sci Technol. 2002; 46(3):105-13**

A general procedure was developed for estimating the concentrations of pharmaceutical residues in fresh primary and secondary sewage sludge. Prescribed quantities coupled with information on the various excretion ratios of 20 pharmaceuticals and 2 of their metabolites enabled prediction of the overall rates of excretion into Australian sewage. Fugacity modelling was applied to predict concentrations of these residues in fresh primary and secondary sludge. Predicted concentrations ranged from 10(-3)-884 microg/L in primary sludge and 10(-4)-36 microg/L in secondary sludge. Overall rates of removal to sludges ranged from 1-39%. The accuracy of the model was verified by comparison to analytical data.

BIODEGRADATION OF PHARMACEUTICAL RESIDUES INVESTIGATED BY SPE-GC/ITD-MS AND ON-LINE DERIVATIZATION

Christian Zwiener[*], Thomas Glauner, Fritz H. Frimmel

Engler-Bunte-Institut, Wasserchemie, Universität Karlsruhe, Engler-Bunte-Ring 9, 76131 Karlsruhe, Germany

email: Christian Zwiener (christian.zwiener@ciw.uni-karlsruhe.de)

[*]Correspondence to Christian Zwiener, Engler-Bunte-Institut, Wasserchemie, Universität Karlsruhe, Engler-Bunte-Ring 9, 76131 Karlsruhe, Germany

Abstract

Solid-phase extraction, on-line derivatization, and measurement by ion trap mass spectrometry (ITD-MS) were used to investigate the biological degradation of pharmaceutical residues (clofibric acid, ibuprofen, diclofenac). The results of the single steps of sample pretreatment and analytical determination are reported. MS/MS measurements were performed on an ITD-MS by selecting collision induced dissociation of the molecular ions (M^+) as parent ions to defined daughter ions. A pilot sewage plant and biofilm reactors operating under oxic and anoxic conditions were run as model systems with synthetic sewage water containing 10 to 50 mg/L dissolved organic carbon (DOC) and pharmaceuticals in concentrations of 10 µg/L. Clofibric acid displayed its persistent character in all cases. The pilot sewage plant and the oxic biofilm reactor showed comparable results for diclofenac and ibuprofen, which both were partly degraded. These results can explain the occurrence of these substances in sewage effluents and in the aquatic environment. A high degree of degradation was found especially for ibuprofen in the oxic biofilm reactor, which was attributed to adaptation of the biofilm to the residue. Two metabolites of ibuprofen could be identified on the basis of their mass spectra and comparison with literature data, *viz.* hydroxyibuprofen and carboxyibuprofen.

REMOVAL OF ANTIBIOTICS FROM SURFACE AND DISTILLED WATER IN CONVENTIONAL WATER TREATMENT PROCESSES

J. Envir. Engrg., Volume 128, Issue 3, pp. 253-260 (March 2002)

C. Adams,[1] M.ASCE; Y. Wang,[2] K. Loftin,[3] and M. Meyer[4]

[1]Mathes Professor, Dept. of Civil Engineering, Univ. of Missouri-Rolla, 202 Civil Engineering Building, Rolla, MO 65409.

[2]Graduate Research Assistant, Univ. of Missouri-Rolla, 202 Civil Engineering Building, Rolla, MO 65409.

[3]Graduate Research Assistant, Univ. of Missouri-Rolla, 202 Civil Engineering Building, Rolla, MO 65409.

[4]Senior Research Scientist, United States Geological Survey, 4500 SW 40th Ave., Ocala, FL 34474.

(Accepted August 13, 2001)

Conventional drinking water treatment processes were evaluated under typical water treatment plant conditions to determine their effectiveness in the removal of seven common antibiotics: carbadox, sulfachlorpyridazine, sulfadimethoxine, sulfamerazine, sulfamethazine, sulfathiazole, and trimethoprim. Experiments were conducted using synthetic solutions prepared by spiking both distilled/deionized water and Missouri River water with the studied compounds. Sorption on Calgon WPH powdered activated carbon, reverse osmosis, and oxidation with chlorine and ozone under typical plant conditions were all shown to be effective in removing the studied antibiotics. Conversely, coagulation/flocculation/sedimentation with alum and iron salts, excess lime/soda ash softening, ultraviolet irradiation at disinfection dosages, and ion exchange were all relatively ineffective methods of antibiotic removal. This study shows that the studied antibiotics could be effectively removed using processes already in use in many water treatment plants. Additional work is needed on by-product formation and the removal of other classes of antibiotics.

PHARMACEUTICALS AND PERSONAL CARE PRODUCTS (PPCPS) IN SURFACE AND TREATED WATERS OF LOUISIANA, USA AND ONTARIO, CANADA

Authors: Boyd G.R.[1]; Reemtsma H.; Grimm D.A.; Mitra S.

Source: The Science of the Total Environment, Volume 311, Number 1, 20 July 2003, pp. 135-149(15)

Publisher: Elsevier Science

Abstract

A newly developed analytical method was used to measure concentrations of nine pharmaceuticals and personal care products (PPCPs) in samples from two surface water bodies, a sewage treatment plant effluent and various stages of a drinking water treatment plant in Louisiana, USA, and from one surface water body, a drinking water treatment plant and a pilot plant in Ontario, Canada. The analytical method provides for simultaneous extraction and quantification of the following broad range of PPCPs and endocrine-disrupting chemicals: naproxen; ibuprofen; estrone; 17b-estradiol; bisphenol A; clorophene; triclosan; fluoxetine; and clofibric acid. Naproxen was detected in Louisiana sewage treatment plant effluent at 81–106 ngyl and Louisiana and Ontario surface waters at 22–107 ngyl. Triclosan was detected in Louisiana sewage treatment plant effluent at 10–21 ngyl. Of the three surface waters sampled, clofibric acid was detected in Detroit River water at 103 ngyl, but not in Mississippi River or Lake Pontchartrain waters. None of the other target analytes were detected above their method detection limits. Based on results at various stages of treatment, conventional drinking-water treatment processes (coagulation, flocculation and sedimentation) plus continuous addition of powdered activated carbon at

a dosage of 2 mgyl did not remove naproxen from Mississippi River waters. However, chlorination, ozonation and dual media filtration processes reduced the concentration of naproxen below detection in Mississippi River and Detroit River waters and reduced clofibric acid in Detroit River waters. Results of this study demonstrate that existing water treatment technologies can effectively remove certain PPCPs. In addition, our study demonstrates the importance of obtaining data on removal mechanisms and byproducts associated with PPCPs and other endocrine-disrupting chemicals in drinking water and sewage treatment processes.

ECOTOXICOLOGICAL IMPACT OF PHARMACEUTICALS FOUND IN TREATED WASTEWATERS: STUDY OF CARBAMAZEPINE, CLOFIBRIC ACID, AND DICLOFENAC

Authors: Ferrari B.; Paxeus N.; Giudice R.L.; Pollio A.; Garric J.[1]

Source: Ecotoxicology and Environmental Safety, Volume 55, Number 3, July 2003, pp. 359-370(12)

Publisher: Elsevier Science

Abstract

In four countries (France, Greece, Italy, and Sweden) occurrence in sewage treatment plant (STP) effluents and ecotoxicity of the pharmaceuticals carbamazepine, clofibric acid, and diclofenac were investigated. Bioassays were performed on bacteria, algae, microcrustaceans, and fishes in order to calculate their predicted no-effect concentrations (PNEC) and to perform a first approach of risk characterization. For this aim, risk has been estimated by the predicted environmental concentration/PNEC ratio and the measured environmental concentration/PNEC ratio. First, regarding the PNEC, carbamazepine appears to be the more hazardous compound. Second, even though it is demonstrated that carbamazepine, clofibric acid, and diclofenac have been detected in effluents, only carbamazepine have been detected in all sewage treatment plants with the greatest concentrations. Third, risk quotients greater than unity were calculated only for carbamazepine, suggesting that risk for the water compartment is expected.

OTHERS

A HUMAN HEALTH RISK ASSESSMENT OF PHARMACEUTICALS IN THE AQUATIC ENVIRONMENT

Lisa J. Schulman , Edward V. Sargent [A1], Bruce D. Naumann [A1], Ellen C. Faria [A1], David G. Dolan [A1], John P. Wargo [A3]

[A1] Merck & Co., Inc., Two Merck Drive, P.O. Box 200, WS2W-13, Whitehouse Station, NJ 08889-0200
[A2] Merck & Co., Inc., 126 E. Lincoln Ave., Rahway, NJ 07065

[A3] Yale University, School of Forestry and Environmental Studies, 135 Prospect Street, New Haven, CT 06511

ELIMINATION OF COD, MICROORGANISMS AND PHARMACEUTICALS FROM SEWAGE BY TRICKLING THROUGH SANDY SOIL BELOW LEAKING SEWERS

Authors: Hua J.; An P.; Winter J.; Gallert C.[1]

Source: Water Research, Volume 37, Number 18, November 2003, pp. 4395-4404(10)

Publisher: Elsevier Science