ABSTRACT

Occurrence and Behavior Analysis of EDCs

in the Sewage Treatment Plant (STP).

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Introduction

In recent decades it has been confirmed that some chemicals found in river water so called EDCs (Endocrine Disrupting Chemicals), are capable to disturb the normal function of the endocrine system, of both humans and wildlife. Many cases of abnormalities in wildlife, particularly those associated with reproductive functions, are suggested to be caused by exposure to EDCs. Natural estrogens, such as 17β -estradiol (E2), estrone (E1), estriol (E3) and their conjugates are considered as EDCs, which are commonly detected in surface water.

Though several free natural estrogens have been detected in municipal STP effluents, there is still a lack of information concerning the behavior of natural estrogens during the STP process. In this study, the measurement of both target estrogens and their conjugates in each steps of the STP process were performed so that the behavior of estrogens during sewage treatment process can be observed. However, since a sufficiently sensitive analytical procedure for detecting estrogen and its conjugate concentration in water requires the use of a sophisticated detection equipment and requires a long and complicated steps of sample preparation, the present study is also aimed to develop a simple and appropriate method to measure estrogens and their conjugates in the environment using LC-MS equipment as an alternative to the more sophisticated LC-MS/MS or GC MS/MS equipments. It is believed by the author that since natural estrogens and their conjugates are not easy to evaporate, LC-MS could be used in the experiment as long as an appropriate sample pretreatment method is employed.

Experimental results and discussions

Two pretreatment methods were proposed in this study, they are: a modification of Snyder method (SM method) and a proposed alternative method (PA method). The methods basically consist of enrichment, extraction and clean up steps. The same clean up step and detection conditions were performed in both methods.

Dichloromethane was used for extraction in SM method and 35% acetone in hexane was used in PA method. The equipment employed for SPE in SM method is shown in Figure A-1 and that employed in PA method is shown in Figure A-2.

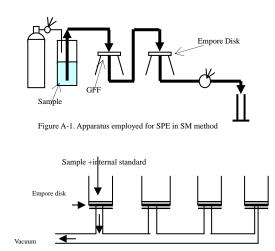


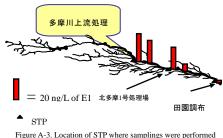
Figure A-2. Apparatus employed for SPE and extraction in PA

The methods were applied on the sewage samples taken from "多摩川上流処理場", an STP located close to Tamagawa river, in which high EDC activities have been observed to raise in area close to the STP and the major portion was detected as estrone. The application of both the SM and PA methods makes it possible to find the advantages and disadvantages of each method. Application of SM method is able to detect BPA better than employed of PA method. However application of PA method increased the ability on the detection of estriol concentrations. The concentrations obtained in the STP are shown in Figures A-4.a. and A-4.b.

A second application was performed to find out the estrogen concentration in the STP with some additional sampling points. PA method was employed in these samples; the measurement results are shown in Figure A-5. It is shown that the patterns of estrogens detected in second samples are similar to the detection results of first samples.

E1 and E2 are increased during aeration, and decrease continuously in the sedimentation tank II and effluent. Transformation of natural estrogens and degradation of conjugates may take an important role during the process. In case of estriol, the elevation was more significant in sedimentation tank II, because some of estriol were produced from a conversion of both estrone and estradiol, which are increased in the aeration tank. The results are also evaluated and compared to the predicted concentration of natural estrogens excreted by the population served by the STP. The predicted concentration is shown in the sources value of Figure A-6. The results strengthened the possibility of conjugates degradation during aeration/ activated sludge process. The quality of effluent from "多摩 川上流処理場" STP is better than that of other STPs in other countries as found in the literature. However still does not give any assurance concerning whether or not the current effluent is safe for wildlife (Figure A-7).

Measurements of natural estrogens content in aquatic organisms and an assessment of the degree of estrogenic disturbances is necessary and is posed as an important further research topic.



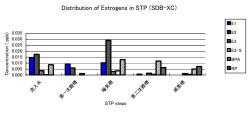


Figure A-4.a. EDCs concentration obtained from first sampling (SM

Distribution of Estrogens in STP (C-18)

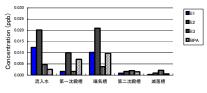


Figure A-4.b. EDCs concentration obtained from first sampling (PA method)

Distribution of EDCs in STP II (C-18)

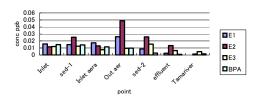


Figure A-5. EDCs concentration obtained from second sampling

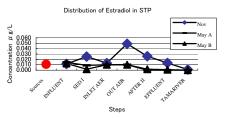


Figure A-6. Comparison of estradiol concentration obtained

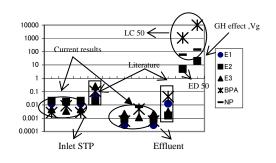


Figure A-7. Comparison of obtained concentration and LC 50 found in