# OCCURRENCE OF MICROPOLLUTANTS IN WASTEWATER AND THE FOUR MAJOR RIVER, KOREA

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## Introduction

Concerns about hazardous micropollutants in streams and rivers have grown because of the potential threat to the health of humans and the ecosystem. Over the last decade, the presence of low concentrations of numerous contaminants (such as pesticides, solvents, and plasticizers) has been reported in surface water throughout the world[1,2]. In Greece and Spain, industrial wastewater containing various micropollutants has been reported as a major source of water pollution in rivers[3,4].

In Korea, the Ministry of Environment has also monitored micropollutants in 4 major rivers and released several reports. In this paper, data about the 4 major rivers in Korea were analyzed and discussed with respect to rainfall characteristics and pollutants from industrial wastewater.

## Materials and methods

The KME report[5] presents the risk assessment results, along with the concentrations of volatile compounds, semi-volatile compounds, and heavy metals. The volatile and semi-volatile compound data in the river water and industrial wastewater were used here. Representatively, the sampling and analytical procedures presented in the Geum River report[5] are briefly summarized below.

The river samples were collected from 14 sites along the Geum River. In addition, samples from industrial wastewater, which represents one of the point sources of rivers, were also collected from 6 sites. The samples were collected on 3 occasions from spring to early summer in 2011; specifically, 24th February to 1st March, 11th April to 15th April, and 21th June to 27th June. The samples were collected in 40-mL and 1-L glass bottles without headspace. The samples were the kept in 4 °C iceboxes in the field and stored in a refrigerator at a temperature between 0 and 4 °C, normally within 24 to 48 h.

The Headspace Solid-Phase Micro Extraction (HS-SPME) coupled with Gas Chromatography/Mass Spectrometry (GC/MS) method was used for analyzing volatile compounds[6]. The sample volume used for the headspace analysis method was 4 mL in a 10-mL vial with 1,2-dichlorobenzene-d4 and fluorobenzene for the internal standard solution. Agilent 6890A gas chromatography with the Agilent 5973N mass spectrometer and the Combipal Autosampler (Headspace-SPME) were used.

An extraction method was used for analyzing semi-volatile compounds[7]. Phenanthrene-d10 was added for the internal standard solution. The samples were extracted using dichloromethane by mechanical shaking. After separating dichloromethane by using a funnel, anhydrous sodium sulfate was added to remove water, and then, it was concentrated in a vacuum rotary evaporator. A volume of 2 μL sample solution was injected into the GC/MS. Agilent 7890A gas chromatography and Agilent 5975B mass spectrometer were used.

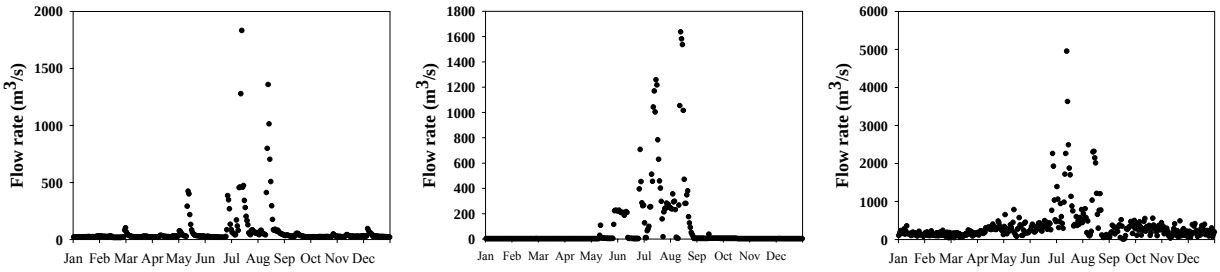
The details of the mean recovery, detection limit, and quality assurance/quality control were presented in previous reports[6,7].

WAMIS data[8] were mainly used to analyze the information and flow rates of the river basin. The description of industrial factories and water use in the Geum River are briefly summarized below. The Daedeok Industrial Complex contains 130 mechanical factories, 39 electric and electronic factories, and 65 chemical factories. This industrial complex covers an area of 3,113,669 $m^2$, with around 11,000 people working in 316 factories. The first and the second Daejeon Industrial Complex primarily contain mechanical factories and petrochemical plants, with 4000 workers in 187 factories. The 2 complexes cover a total area of 1,256,000 $m^2$. The Hyundo Industrial Complex is the smallest of the 6 complexes. Finally, the Cheongju Industrial Complexes contain 115 electric and electronic factories and 84 mechanical factories. These industrial complexes cover an area of 4,098,000 $m^2$, with around 26,000 people working in 358 factories. Most of the water used in farming (2,210,631,700 m3/year) was used for rice farming (75.5%), with the remainder being used for dry field farming (23.2%) and the livestock

industry (1.3%). Livestock farming consisted of beef cattle (287,255 heads), dairy cattle (39,678 heads), pigs (909,021 heads), and poultry (18,256,282 heads).

**Results and discussion**

The rivers in Korea have certain interesting characteristics. First, the rivers are relatively shorter than other rivers across the world. Second, the channels have high slopes (banks) because of steep mountains and deep valleys. Finally, the basins are smaller than other basins across the world. Moreover, in Korea, 40–60% of annual rainfall characteristically occurs during summer (July-September). Therefore, the flow rate also varies because of heavy rain during the short summer period. Figure 1 presents the change in river flow rate with rainfall in the Geum River during 2011.




< Okcheon > < Maepo > < Guam >

Fig. 1. Change in the rate of flow at the 3 rain gauge stations along the Geum River in 2011.

*Pesticides*

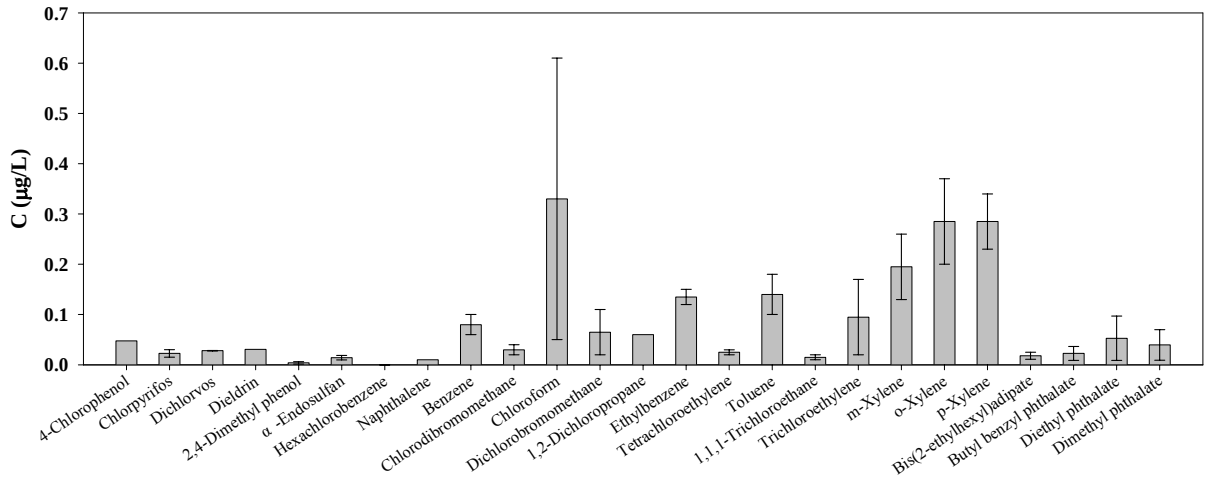
The river water was tested for the presence of 24 pesticides in Geum River. In total, 9 pesticides were recorded during the study period: 4-chlorophenol, chlorpyrifos, 1,2-dichlorobenzene, dichlorvos, dieldrin, 2,4-dimethylphenol, α-endosulfan, hexachlorobenzene, and naphthalene. 4-Chlorophenol, 2,4-dimethylphenol, and hexachlorobenzene were detected on all 3 sampling occasions in the river. A wide range in the concentration of pesticides was recorded in the river across the sampling period, ranging from $10^{-5}$ μg/L to $10^{-2}$ μg/L. However, the general concentration level for most detected pesticides was $10^{-2}$ μg/L. Only the concentration range of hexachlorobenzene varied from $10^{-5}$ μg/L to $10^{-4}$ μg/L. The average frequency of all the detected pesticides during February was 32.1%. The frequency of 2,4-dimethylphenol and hexachlorobenzene was much higher than that of the other pesticides detected during the sampling period.

In comparison, the pesticides recorded in the wastewater were 4-chlorophenol, 1,2-dichlorobenzene, dichlorvos,1,4-dichlorobenzene, 2,4-dimethylphenol, hexachlorobenzene, and naphthalene. 2,4-Dimethylphenol, hexachlorobenzene, and naphthalene occurred at all 3 sampling events, while 4-chlorophenol was detected during April and June only. The wastewater pesticide concentrations varied widely from $10^{-5}$ μg/L to $10^{-1}$ μg/L. However, the general concentration level of most detected pesticides was $10^{-2}$ μg/L as that in the river water. 2,4-Dimethylphenol and naphthalene were mostly observed at the highest concentrations. The site with the greatest range in pesticides in the wastewater differed in each sampling month. Three compounds were found at the treated wastewater from Cheongju Industrial Complexes in February. In particular, naphthalene occurred in every sampling month in the wastewater and had the highest intensity at the treated wastewater from the second Daejeon Industrial Complex and the Daedeok Industrial Complex.

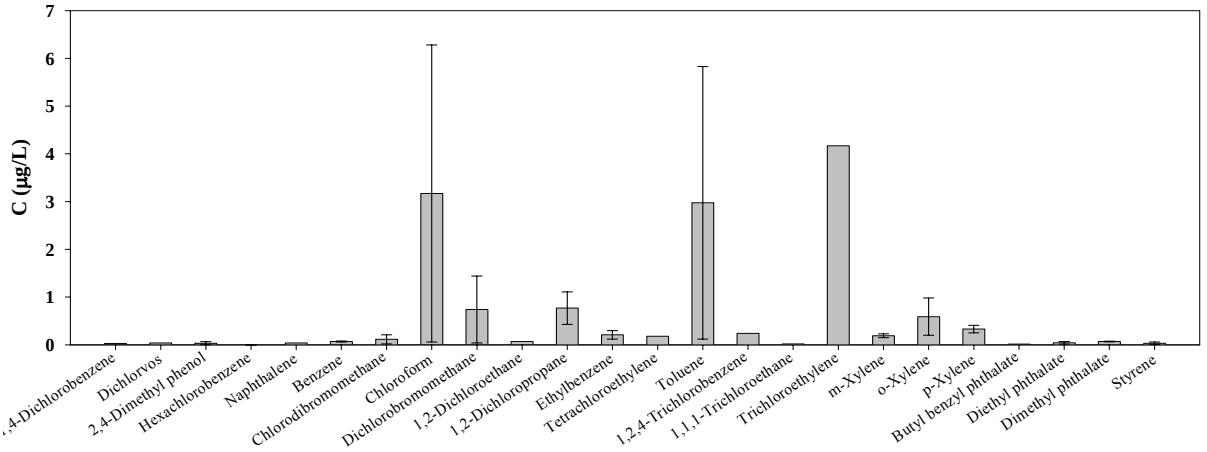
*Solvents*

The river was tested for a total of 28 solvents, of which 14 were detected; specifically, benzene, bromoform, chlorodibromomethane, chloroform, dichlorobromomethane, 1,2-dichloropropane, ethylbenzene, tetrachloroethylene, toluene, 1,1,1-trichloroethane, trichloroethylene, m-xylene, o-xylene, and p-xylene. In February, 13 of the solvents were detected. In particular, benzene, chlorodibromomethane, dichlorobromomethane, ethylbenzene, toluene, m-xylene, o-xylene, and p-xylene were recorded in all 3 sampling months. The solvent concentration levels in the river ranged from $10^{-2}$ μg/L to $10^{0}$ μg/L, with an general concentration level of $10^{-1}$ μg/L. High concentrations of benzene, ethylbenzene, toluene, m-xylene, o-

xylene, and p-xylene were recorded. In comparison, low concentrations of chlorodibromomethane were recorded compared to the other detected solvents in the river during the sampling period. The average frequency of the solvents detected in February in the river was 59.9%. In particular, the frequency of o-xylene and p-xylene was 100% in all 3 sampling months, compared to the other 6 solvents also detected in all 3 months.




* Not detected compounds (Pesticides: acrolein, acrylonitrile, 1,2-dibromo-3-chloropropane, 1,2-dichlorobenzene, 1,4-dichlorobenzene, 1,3-dichloropropylene, dinoseb, β-endosulfan, heptachlor, heptachlor epoxide A, heptachlor epoxide B, methoxychlor, methyl bromide, 3-methyl-4-chlorophenol, 2-methyl-4,6-dinitrophenol, 4-nitrophenol; Solvents: bromoform, n-butylbenzene, chlorobenzene, 1,3-dichlorobenzene, 1,1-dichloroethane, 1,2-dichloroethane, 1,1-dichloroethylene, 1,2-cis-dichloroethylene, 1,2-trans-dichloroethylene, epichlorohydrin, hexachlorobutadiene, methyl chloride, 1,1,2,2,-tetrabromoethane, 1,2,4-trichlorobenzene, 1,1,2-trichloroethane; Plasticizers: di-n-butyl phthalate, 2,4-dinitrotoluene, 2,6-dinitrotoluene, di-n-octyl phthalate; Others: acrylamide, 2,4-dinitrophenol)




* Not detected compounds (Pesticides: acrolein, acrylonitrile, 4-chlorophenol, chlorpyrifos, 1,2-dibromo-3-chloropropane, 1,2-dichlorobenzene, 1,3-dichloropropylene, dieldrin, dinoseb, α-endosulfan, β-endosulfan, heptachlor, heptachlor epoxide A, heptachlor epoxide B, methoxychlor, methyl bromide, 3-methyl-4-chlorophenol, 2-methyl-4,6-dinitrophenol, 4-nitrophenol; Solvents: bromoform, n-butylbenzene, chlorobenzene, 1,3-dichlorobenzene, 1,1-dichloroethane, 1,1-dichloroethylene, 1,2-cis-dichloroethylene, 1,2-trans-dichloroethylene, epichlorohydrin, hexachlorobutadiene, methyl chloride, 1,1,2,2,-tetrabromoethane, 1,1,2-trichloroethane; Plasticizers: bis-(2-ethylhexyl)adipate, di-n-butyl phthalate, 2,4-dinitrotoluene, 2,6-dinitrotoluene, di-n-octyl phthalate; Others: acrylamide, 2,4-dinitrophenol)

Fig. 2. Occurrence of pesticides, solvents, plasticizers, and other compounds in the river water (up) and the treated industrial wastewater (down) during February 2011, Geum River. (unit: µg/L)

Seventeen solvents were detected in the wastewater during the sampling period, specifically, benzene, bromoform, chlorobenzene, chlorodibromomethane, chloroform, dichlorobromomethane, 1,2-dichloroethane, 1,2-dichloropropane, ethylbenzene, tetrachloroethylene, toluene, 1,2,4-trichlorobenzene, 1,1,1-trichloroethane, trichloroethylene, m-xylene, o-xylene, and p-xylene. Fifteen of the solvents were recorded in February. Eleven of the solvents occurred in all 3 sampling events, specifically, benzene, chlorodibromomethane, chloroform, dichlorobromomethane, ethylbenzene, tetrachloroethylene, toluene, trichloroethylene, m-xylene, o-xylene, and p-xylene. The concentrations of solvents in the wastewater ranged from $10^{-2}$ μg/L to $10^{0}$ μg/L. Chloroform, toluene, and trichloroethylene were detected in all 3 sampling months at concentrations of $10^{0}$ μg/L, which was the highest level of all detected compounds. Benzene, ethylbenzene, m-xylene, o-xylene, and p-xylene were also detected at all the sampling sites, with a concentration range of $10^{-2}$–$10^{-1}$ μg/L. The average frequency of all detected solvents during February was 65.6%. The frequency of benzene, ethylbenzene, m-xylene, o-xylene, and p-xylene was 100% on all occasions; in other words, these 3 compounds were detected every time at all industrial complexes. Chloroform and toluene also had one of the highest frequencies in the wastewater. The number of compounds that occurred at a specific site varied from 6 to 12.

*Plasticizers*

This study tested for the presence of 8 plasticizers, of which 4 were detected, specifically, bis-(2-ethylhexyl) adipate, butyl benzyl phthalate, diethyl phthalate, and dimethyl phthalate. All 4 plasticizers were found in all 3 sampling months. The range in plasticizer concentrations in the river water was $10^{-3}$–$10^{-2}$ μg/L, which was relatively stable. The highest concentrations of plasticizers in all 3 sampling months in the river were those of diethyl phthalate and dimethyl phthalate. The average frequency of all detected plasticizers in the river during February were 57.2%. Diethyl phthalate and dimethyl phthalate were found at the highest frequency in the river.
Four plasticizers were detected in the wastewater, which were similar to the compounds detected in the river. Diethyl phthalate and dimethyl phthalate were detected in all 3 sampling months and at all wastewater sites. The concentration of plasticizers in the wastewater ranged from $10^{-3}$ μg/L to $10^{-1}$ μg/L; however, the general concentration level of plasticizers was $10^{-2}$ μg/L. The average frequency of plasticizers in February was 38.9%. Diethyl phthalate consistently occurred at most sites.

**Acknowledgements**

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