공학석사 학위논문

Determination of site-specific acceptable concentrations of copper using fixed monitoring benchmarks in water: Soil porewater and stream water

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fixed monitoring benchmarks와 독성영향인자
시계열 데이터 활용 기법에 관한 연구

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2018 년 2 월

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Abstract

Determination of site-specific acceptable concentrations of copper using fixed monitoring benchmarks in water : Soil porewater and stream water

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Biotic ligand model (BLM) has been used widely to predict Cu concentration in water that affects 50% of species (50% effective concentration, EC50) with site-specific water characteristics to assess its toxicity ecotoxicologically. It, however, has a limitation that its predicted Cu concentrations change over time because the characteristics of water varies. To determine a site-specific acceptable Cu concentration from varying BLM predictions, the fixed monitoring benchmarks which is a probability based method was introduced. It assesses the compliance of dissolved Cu concentrations in the site water with the BLM-predicted instantaneous water quality criterion(IWQC) and determines the highest acceptable concentration of dissolved Cu that the site water may reach potentially by probability. Soil porewater samples collected from Janghang city, Republic of Korea, during the 5 months of sampling period showed

their characteristics including pH, DOC, temperature and cation concentrations changed each time when sampled. That resulted in different BLM-predictions over the period and based on the probability, the Cu concentrations in this site are expected to exceed the BLM-predicted safe concentrations more frequent than once in three years. In order to make its concentrations to be in compliance with the BLM predictions, the maximum dissolved Cu concentration it should reach is determined to be 0.17 mg/L to protect barley and local plants in the region.

To expand the concept of FMB to spatially different locations, it was applied to stream waters within Han River basin with 12 different monitoring stations in Korea. Each station had different water characteristics from June 2014 to October 2016 which resulted in different BLM-predicted IWQC regionally. When the dissolved Cu^{2+} concentration and the Ca^{2+} concentration were assumed to be identical in each station, the predicted copper FMB values differed up to 95% in 12 stations from 2.63 to 7.41 μg/L. Current water quality monitoring system in Korea does not measure cation concentrations and measure Cu concentrations only at selective sites. Ca^{2+} itself is not a hazardous contaminant in water but it affects the toxicity of copper when dissolved in water. It changes the copper FMB from 3.999 to 28.87 μg/L when the Ca^{2+} concentration changes from 0 to 2 mM. The distribution of dissolved Cu^{2+} concentrations also affect the copper FMB values from 4.30 to 23.7 μg/L when the standard deviation of the distribution differs 1, 1.1, 1.2, 1.3, 1.4 and 1.5. The predicted copper FMB values are very sensitive to the dissolved Ca^{2+} concentrations and Cu^{2+} concentrations in water and to make the predictions more accurately, it is important to measure Ca^{2+} and Cu^{2+}

concentrations in monitoring system in Korea.
Key words: Biotic ligand model, Fixed monitoring benchmarks, copper toxicity, soil porewater
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1. Introduction

1.1 Background

A concept of bioavailability in environmental science suggested a new methodology of determining ecotoxicological criteria for heavy metals in contaminated soil and water. In the past the total concentration of heavy metal in the environmental media was thought to be hazardous to living organisms and therefore when determining heavy metals' regulatory criteria their total concentrations mattered. Bioavailability, however, explains that only a dissolved form of the total concentration in the metals is available to be adsorbed to organisms and hence reveals toxic effects to them. Such metal toxicity in water varies greatly as environmental factors change. Ion concentrations, pH and dissolved organic carbon (DOC) are major factors determining heavy metal toxicity in water system meaning that its toxicity would not be same to different organisms. Instead it will change according to the surrounding conditions even though the total concentration of the metal remains the same.

The Biotic Ligand Model concept (BLM) was introduced to explain metal speciation and complexation in solution with regard to its toxicity revealing to living organisms (Di Toro et al.,2001). The basic concept of it was based on previous a giill surface interaction model (Pagenkopf, 1983) and a free ion activity model of toxicity (Campbell, 1995) that free metal ion interacts on fish gill and giving toxic effects to the fish. The BLM expands this idea to be applicable to more aquatic organisms assuming that free metal ions bind to an active binding site called the biotic ligand. Not the total concentration of the metal but only a fraction of it is available to bind to the biotic ligands revealing the toxic effects. The BLM is site-specific because the fraction of available free metal ions depends on the site characteristics including cation concentrations, pH and DOC. The free metal ions form complexes with both organic and inorganic matters in solution and those complexes become unavailable to the biotic ligands decreasing toxic effects. In the meantime cations also compete with the free metal ions for the limited number of botic ligand thus inhibiting them to bind (Di Toro et al.,2001). These binding sites can be either physiologically active sites, causing a direct biological response, or transport sites, causing metal transport into the cell which is followed by a subsequent, indirect biological response (Lock et al., 2007).

The first BLM was developed to predict the toxicity of metal in aquatic organisms and then the terrestrial biotic ligand model (TBLM) was proposed by Thakali et al.,(2006) which is applicable to soil porewater. Its main assumption is that free heavy metal ions in soil porewater bind to the active binding site of the terrestrial living organisms. In addition the DOC present in porewater decreases the number of free heavy metal ions as it forms complexes with them and thus decreases their toxic effects (An et al., 2015).

To evaluate the effect of heavy metal toxicity to organisms, the BLM has been widly used and the U.S. EPA also provided copper water quality criteria using BLM (U.S. EPA 2007)(11). The BLM has been applied to predict copper toxicity to fish and invertebrates in freshwater with various environmental factors in several states in the USA and European countries. The environmental factors, however, change instantaneously which leads to different BLM predictions from sample to sample even though they are collected from the same sampling station. Thus the necessity for introducing a new method interpreting such time variability was demanded in order to make the BLM available to be used as a tool for determining water quality criteria. Such problem with regard to time variability is not limited to the BLM. The hardness equation which has been used for water quality criteria ahead of the BLM in the USA (U.S. EPA 1985a) also has the same limitation. Ever since 1980s when the hardness equation was first introduced, the issue with time variability and changing water quality criteria followed. In such case when the criteria yield different numbers, they were simply averaged to give a single and constant criteria. The BLM was introduced in 2001 suggesting important parameters in determining heavy metal toxicity which were not considered in the previous hardness equation such as pH, DOC and ion concentrations in environmental media that are consistently time-variable. To deal with this limitation the BLM has, a new concept of incorporating the BLM and time variability based on a probability method was proposed by HydroQual(2008). With varying BLM-predicted metal concentrations over time, it evaluates if the concentration of metal in site water is in compliance with the BLM-predicted concentration (instantaneous water quality criterion, IWQC). If the current metal concentration exceeds the IWQC more frequent than once in three years of exceedance frequency, the metal concentration in site water should decrease until it satisfies the BLM predictions to be protective of organisms in the area.

Prediction models for metal toxicity has improved during the past years. Hardness concentration based metal criteria had been used since 1985 by National Ambient Water Quality Criteria from the USEPA to predict their toxicities in water assuming that the hardness in water would affect them the most. Then the concept of water effect ratio (WER) was introduced to determine the site-specific metal toxicity more easily because the previous model required the toxicity tests each time. Conducting the experiments every time was not viable therefore WER, which is a ratio of the toxicity test result in the site to the toxicity test result in the lab, replaced the large scale experiment in the site and enabled to find a site-specific water quality criteria by multiplying this ratio to the lab test results. Then the BLM was developed and considered the bioavailability of metal which is highly dependent on water chemistry at the site when determining their toxicity. The BLM predicts the metal toxicity that is ecotoxicologically safe to the living organism. These models, however, had a limitation that their prediction values are time-variable. The water chemistry data they used were changing over time which resulted in different predictions. Using the averaged value of the parameter did not yield the reasonable criterion of the site. Therefore a new method incorporating the time variability and the prediction model was in need and the fixed monitoring benchmarks (FMB) was introduced.

In this study, an acceptable copper concentration will be predicted in Korean water using the FMB. Copper is a heavy metal commonly found in water because of both naturally occurring reason and anthropogenic contamination. When it is present at low concentrations, it could be an essential nutrient for plants and animals but toxic to organisms in aquatic environment. Thus it is important to monitor if the copper concentration exceeded the background concentration in water and predict at what concentration it would change from non-toxic to toxic. In addition currently in Korean water quality monitoring system copper is not measured at most monitoring stations despite the toxicity it may have potentially under certain environmental conditions. Therefore the prediction of the acceptable copper concentration that is safe enough to living organisms would be necessary to protect the ecosystem. The current criterion of permissible emission concentration of copper in stream water is 3 mg/L which is applied for the entire stream water in Korea without considering their site-specific circumstances and the local organisms that may have influence from it biologically.

1.2 Research objectives

The objective of this research is to apply fixed monitoring benchmarks method to water in order to find a site-specific acceptable concentration of Cu.

(1) Soil porewater

This study aims to collect water chemistry information from direct porewater sampling from Jun 2017 to November 2017 at Janghang site in order to check the influence of water chemistry change over the sampling period to the prediction of an acceptable copper concentration. This copper concentration would be ecotoxicologically protect barley and a few local plants in the area.

(2) Stream water

With water quality data obtained using database, different acceptable copper concentrations from 12 stream water monitoring stations within Han River basin were predicted. Also the study checked the availability of applying the fixed monitoring benchmarks to the current water quality monitoring system.

1.3 Research area

The study selected two different types of water to find an acceptable copper concentration in the region.

(1) Soil porewater

Janghang, a small city located in the middle of S.Korea and southern of Seoul was chosen because it is known as heavy metal contaminated area and remediation project is on going as a part of risk assessment process. There had been a smelter in this site for 53 years and both air pollution and soil contamination are at risk level giving a hazard to the local population. Therefore applying the fixed monitoring benchmarks in this site to predict an ecotoxicoloically acceptable copper concentration would provide a good guildline to introduce this method to other contaminated areas.

(2) Stream water

There are four river basins in S.Korea and Han River basin includes the regions near Seoul, the capital. It has provided water sources to people in capital more than 500 years for drinking and many other purposes. Currently 23 monitoring stations are placed in streams which belong to Han River, and 12 of them are chosen in this study for determination of acceptable copper concentration. The selected stations are spatially distributed within the basin and expected to have variations in environmental factors monitored from June 2014 to October 2016.

2. Literature review

2.1 Bioavailability and copper toxicity

2.1.1 Bioavailability

Bioavailability is a measure of fraction a chemical is transferred from environmental media to an organism at its specific internal site. Often this transfer is not simply proportional to the total chemical concentration in the environment, but varies according to attributes of the organism, chemical, and exposure environment so that the chemical is more or less “bioavailable” (USEPA, 2007). Because the rates of chemical species being transferred into the organism differ depending on complexation and speciation of the chemical, the fraction of bioavailable form from the chemical to the organism would not be proportional to the total concentration of metal but different depending on the characteristics of the environmental media such as water or soil. With the bioavailability concept, the toxicity of metals could be explained that it occurs because of the free metal ion reacting with the physiologically active binding sites at the organism which is in bioavailable form (Di Toro et al., 2001).

2.1.2 Copper toxicity

For copper, a small fraction of it exists as cupric ion (Cu^{2+}) and the most of them are in other forms either forming complexes with organic compounds, hydroxides or inorganic matter etc. Therefore the copper toxicity has been reported to vary markedly due to various physicochemical characteristics of the exposure water, including temperature, dissolved organic compounds, suspended particles, pH, and various inorganic cations and anions, including those composing hardness and alkalinity (USEPA, 2007).

2.2 Biotic ligand model (BLM)

2.2.1 Main assumptions of BLM

Biotic ligand model(BLM) has two main assumptions. One of them is that free metal ion binds to active binding site, known as biotic ligand(BL), and reveals toxic effects to the organism. Secondly the major cations just as Ca^{2+}, Mg^{2+}, Na^{+} and K^{+} may compete with free metal ions for the limited number of binding site and thus decrease toxic effects.

2.2.2 Mathematical description of BLM

The model was developed to predict metal toxicity to aquatic organisms originally and its concept expanded to a terrestrial model assuming dissolved forms of metal in soil porewater would also be bioavailable to the terrestrial organisms. For a terrestrial BLM predicting Cu toxicity in *Hordeum Vulgare*, Thakali et al,(2006) proved cations H^{+}, Ca^{2+}, and Mg^{2+} compete with free heavy metal ions for limited BL sites and reduce metal toxicities by inhibiting their bind to BL. Therefore the total BL site concentration, [TBL], is given as the equation (1) below.

$$[TBL] = [BL^-] + [HBL] + [CaBL^+] + [MgBL^+] + [MBL^+] \qquad (1)$$

Using the equilibrium relationship

$$\frac{[X_i BL]}{[BL^-][X_i]} = K_{XBL} \qquad (2)$$

The equation (1) could be written as

$$[TBL] = [BL^-](1 + K_{HBL}\{H^+\} + K_{CaBL}\{Ca^{2+}\} + K_{MgBL}\{Mg^{2+}\} + K_{MBL}\{M^{2+}\}) \qquad (3)$$

The toxicity of heavy metal could be predicted by f, the fraction of BL sites occupied by free heavy metal ion, is calculated as the equation (4). At BL sites, cations (i.e., Ca^{2+}, Mg^{2+}, K^+, Na^+, H^+) may compete with free heavy metal ions for limited BL sites which results in a decrease of toxicity.

$$f = \frac{[CuBL^+]}{[TBL]} = \frac{K_{CuBL}\{Cu^{2+}\}}{1 + K_{CuBL}\{Cu^{2+}\} + K_{HBL}\{H^+\} + K_{CaBL}\{Ca^{2+}\} + K_{MgBL}\{Mg^{2+}\}} \qquad (4)$$

Therefore the activity of M^{2+} resulting in 50% inhibition of root growth from equation (4) is written as

$$EA_{50}\{Cu^{2+}\} = \frac{f_{50}(1 + K_{HBL}\{H^{+}\} + K_{CaBL}\{Ca^{2+}\} + K_{MgBL}\{Mg^{2+}\})}{(1 - f_{50})K_{CuBL}} \quad (5)$$

For BLM predicting heavy metal toxicity to *Daphnia magna*, one of cladocerans, a modified BLM equation by Wang et al.(2012) was used in a condition with solution pH higher than 7.0 because inorganic complexes $CuOH^{+}$ and $CuCO_3$(aq) also reveal toxic effects.

$$f = \frac{K_{CuBL}\{Cu^{2+}\} + K_{CuOHBL}\{CuOH^{+}\} + K_{CuCO_3BL}\{CuCO_3)(aq)\}}{1 + K_{CuBL}\{Cu^{2+}\} + K_{HBL}\{H^{+}\} + K_{CaBL}\{Ca^{2+}\} + K_{MgBL}\{Mg^{2+}\} + K_{CuOHBL}\{CuOH^{+}\} + K_{CuCO3BL}\{CuCO_3(aq)\}} \quad (6)$$

$$EA_{50}\{Cu^{2+}\} = \frac{f_{50}(1 + K_{HBL}\{H^{+}\} + K_{CaBL}\{Ca^{2+}\} + K_{MgBL}\{Mg^{2+}\})}{(1 - f_{50})(K_{CuBL} + K_{CuOHBL}K_{CuOH}\{OH^{-}\} + K_{CuCO3BL}K_{CuCO3}\{CO_3^{2-}\})} \quad (7)$$

BLM parameters used in this study are indicated in a table below.

Table 2.1. BLM parameters for *Horadeum vulgare* and *Daphnia Magna* used in different studies

Species	Endpoint	Log K_{XBL}(L/mol)[a]								f_{50}	Reference
		Toxic species			Major cation						
		Cu^{2+}	$CuOH^{+}$	$CuCO_3$ (aq)	H^{+}	Ca^{2+}	Mg^{2+}	K^{+}	Na^{+}		
Hordeum vulgare	4 d root elongation EC50	7.41	NR[b]	NR[b]	6.48	NA[c]	NA[c]	NA[c]	NA[c]	0.05	Thakali et al. (2006)
Daphnia magna	48 h immobilization EC50	8.02	7.45	7.01	5.40	3.47	3.58	NA[c]	3.19	0.47	De Schamphelaere et al. (2002)

[a] Binding constant between Cu species or major cations and biotic ligand in cell membrane of organism.

[b] NR = not reported.

[c] NA = not affected.

2.3 Fixed monitoring benchmarks (FMB)

2.3.1 Procedures of FMB

Even though BLM predictions consider site-specific environmental factors in the site such as pH, DOC or ion concentrations, they change over time which results in a different BLM prediction each time. HydroQual(2008) suggested a new method to determine a single value as a copper criterion in the specific site when BLM predictions change. The method incorporates the time variability both in the BLM predictions, which is written as instantaneous water quality criteria (IWQC), and actual Cu concentrations in stream water. Because the characteristics of site water varies instantaneously, the term "fixed monitoring benchmarks (FMB)" explains the approach better than "fixed site criteria" as it evaluates if the current Cu concentration were in compliance with IWQC. This approach yields a single number as a Cu criterion which is called FMB and it is different from the previous BLM predictions or IWQC because it considers the Cu concentration from site water whereas the IWQC is independent of it.

HydroQual(2008) introduces the FMB as a value that will produce the same toxic unit distribution exceedance frequency as the time variable IWQC would produce for a given monitoring dataset and explains the method as following. This approach depends on the distribution of toxic units (TU) :

$$TU_i = \frac{Cu_i}{IWQC_i} \tag{8}$$

where TU_i is a single TU value for a single sample collected at time

i, Cu_i is the actual Cu concentration in site water for this sample, and $IWQC_i$ is the BLM predicted safe concentration of Cu for this sample. In order to calculate $TU_{i,}$ the IWQC should be calculated based on the BLM equation with BLM input parameters and the Cu concentration in site water needs to be measured for each sample. Then TU values from each sample form a distribution which enables to estimate the probability whether the Cu concentration in site water exceeds the IWQC or not. This could be written as a probability that TU$\geq$ 1. The approach not just tells whether the current Cu concentrations in site water exceed the IWQC but also determines the Cu concentrations that are in compliance with the IWQC predicted based on the BLM. Such Cu concentrations in compliance (i.e., $Cu_{i,comp}$) may be higher or lower than the original Cu concentrations in site water (Cu_i) and that would depend on the Cu_i and a target exceedance frequency (EF). The target EF is once in three years in HydroQual(2008) as recommended by the water quality criteria guidance document by USEPA but other EFs can be used as well. The USEPA suggested once in three years because it takes about three years in average for natural system to recover when exceedance occurs. The distribution of $Cu_{i,comp}$ can be estimated from the distribution of Cu_i and the target EF, which is once in three years in this analysis. If the probability that TU_i $\geq$1 is less frequent than the target EF, it means that the Cu concentrations in site water does not exceed the BLM-predicted IWQC during the target EF. Thus the Cu concentrations in this site could be alleviated a bit and that yields $Cu_{i,comp}$ greater than Cu_i. On the other hand in case the probability that $TU_i \leq$ 1 is greater than the target EF, the $Cu_{j.}$ would be greater than $Cu_{i,comp}$. When estimating $Cu_{i,comp}$ its standard deviation of log-transformed $Cu_{i,comp}$ is assumed to be equal to the that of Cu_i. To be more specific, the probability that TU_i at the target EF(TU_{EF})≥ 1 is important to evaluate whether the Cu_i. exceeds the IWQC more frequently than the target EF of once in three years. In this analysis of finding FMB value for copper toxicity, EF was set as once in three years which is 1 day out of 1095 days yielding 0.000913 as a frequency. This indicates that the distribution of TU should not have values TU_i > 1 more frequent than 1 day out of 1095 days or 0.000913. In other words TU_i should be less than 1 99.91% of the time during three years of period. Therfore when the TU distribution is plotted in a probability plot, the target EF would be the vertical line at 99.91% and the distribution should cross this at 1 or less for Cu concentrations in site water to be in compliance with IWQC, which is the BLM-predicted safe Cu concentration. From the plot, the TU value at the specified EF could be calculated mathematically as the equation (9).

$$TU_{EF} = 10^{[z_{EF} * s_{TU} + \log_{10}(TU_{Median})]} \tag{9}$$

where Z_{EF} is the number of standard deviations using a standard normal distribution, s_{TU} is the standard deviation of the log-transformed TU values, and TU_{Median} is the median value of TU. Z_{EF} is 3.117 from standard normal distribution having the probability of 1/1095 or 0.000913. Depending on the calculated value of TU_{EF} whether it is greater or less than 1, the TU distribution could be adjusted to have the TU_{EF} of 1. Then it is possible to estimate the new distribution of Cu concentrations, which are in compliance with IWQC, through increasing or decreasing the previous Cu distribution by how much the TU distribution is adjusted. It is called $Cu_{i,\ comp}$ in the following equation. This is a concentration adjusted from Cu concentration in site water and calculated by multiplying an adjustment factor (AF) :

$$AF = \frac{1}{TU_{EF}} \tag{10}$$

and

$$Cu_{i,comp} = Cu_i * AF \tag{11}$$

With $Cu_{i,\ comp}$ it is possible to find the compliant TU distribution which is composed of Cu concentrations in compliance with IWQC and has TU_{EF} = 1 by following equation:

$$TU_{i,comp} = \frac{Cu_{i,comp}}{IWQC_i} \tag{12}$$

The acute FMB is a value that the revised Cu distribution ($Cu_{i,\ comp}$) at the specified EF of 99.91% :

$$FMB_a = 10^{[Z_{EF} * s_{Cu} + \log_{10}(Cu_{Median,comp})]} \tag{13}$$

where $Cu_{Median,comp}$ is the median value of the compliant Cu distribution, and s_{Cu} is the log-transformed standard deviation of the original Cu distribution.

2.4 Species sensitivity distribution (SSD)

2.4.1 Background of SSD

In general bioassay for toxicity test within laboratory is performed with one species and thus it provides species-specific results. However various species exist in natural system and when exposed to the same toxic matter they react differently (Posthuma et al., 2002). Therefore additional data for toxicity test is required to evaluate the toxic effect of the matter and reduce errors from different response by mulitple species.

Species sensitivity distribution (SSD) is a cumulative distribution function that indicates the toxic effect influencing a population of species by single or multiple contaminants. Typically the left tail of the distribution is cut at 5~10% and the concentration protecting 90~95% of the population is determined (i.e., 5% hazardous concentration, HC5). Van Straalen and Denneman (1989) suggested a method finding HC5 through extrapolation based on bioassay data performed independently and it is useful because the species available for toxicity test in the laboratory is limited compared to entire species existing in nature.

Probability density function (PDF) is generated from NOEC (i.e., No observed effective concentration) or ECx (x% effective concentration) as an independent variable by tested species.

$$f(x) = \frac{\exp\left(\frac{\mu - x}{\beta}\right)}{\beta\left[1 + \exp\left(\frac{\mu - x}{\beta}\right)\right]^2} \tag{14}$$

where, $\mu =$ the mean of the distribution

$\beta = \dfrac{S_m\sqrt{3}}{\Pi} =$ a measure of the width of the distribution

$X_m =$ the mean of NOEC or EC_x values

$S_m =$ the standard deviation of NOEC or EC_x values

By integrating the PDF, cumulative density function (CDF) is generated as follow:

$$CDF = \int_{x_1}^{x_2} f(x) \tag{15}$$

With CDF, the concentration influencing 5% of the species population is found within safety range protecting the rest 95% (i.e., $\int_{-\infty}^{\ln HC5} f(x)dx = 0.05$). Therefore by applying SSD, it is possible to estimate the range of concentration protecting various species in nature based on limited species in laboratory and analyze sensitivity to contaminants between different species.

3. Materials and method

3.1 Materials

3.1.1 Porewater sampling

Porewater samples were collected from Janghang heavy metal contaminated site where remediation process is on going since 2016. A smelter in Janghang which was built in 1936 had been run more than 50 years to refine gold, copper and lead and caused severe soil contamination in the area. It once produced 15,000 tons of copper and lead when it was actively operated. Even though it brought wealth and economic stimulus, the smelter contaminated air and soil in the area severely by emitting enourmous amount of dust containing heavy metals. The contaminants are mostly heavy metals including As, Cu, Pb, Zn, Ni and Cd that pollute not only environment but also impose serious health risk to humans when exposed for long term. When the soil samples taken from this site were tested, it exceeded the hazard level given by risk assessment and has potentials of causing carcinogenic effects when exposed to organisms. It was expected that porewater from this site may have dissolved heavy metal concentrations in it and this sampling site was selected to determine a site-specific and ecotoxicologically acceptable copper concentration protecting local plants. From June 11 to November 15 in 2017, 10 samples were collected. The sampling was done twice a month to observe a variability of ion concentrations in time series during this period.

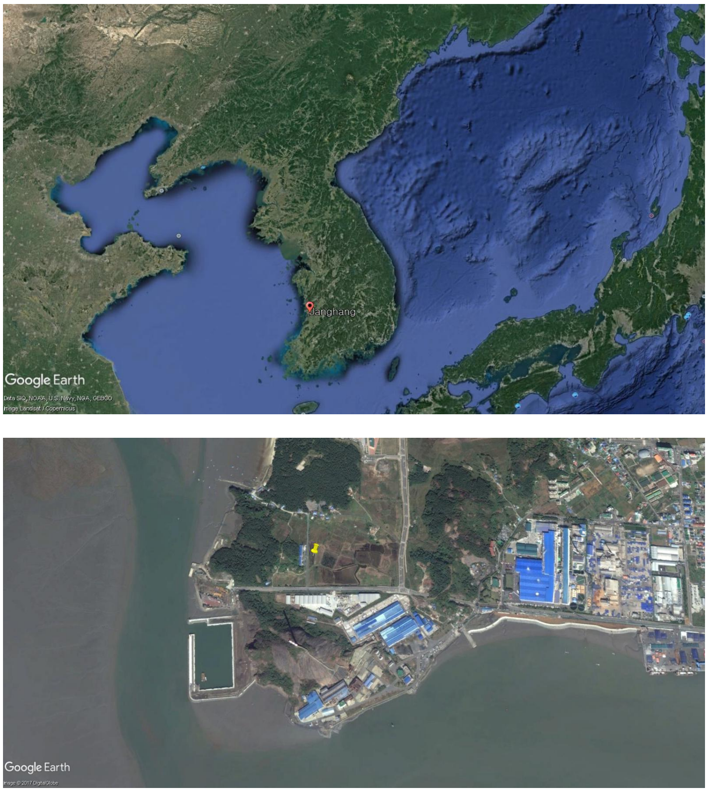


Fig 3.1. Sampling site, Janghang city, Seocheon, Chungcheongnamdo, Republic of Korea

3.1.2 Porewater sampler

Samplers were purchased from (SICS20, UMS, Germany) and placed under the soil with a 10cm depth to fully cover the porous ceramic part. A motor vacuums inside the sampler making it to be under -0.5 bar and due to the pressure difference between the inside and the outside of the sampler, the water is sucked into the equipment. In total of 9 samplers were placed in Janghang site to collect sufficient amount of porewater from each sampling. The more rainfall there was at the site, the more porewater obtained as it saturated soil and helped metals to leach. The collected water was sampled with a syringe and 50mL conical tubes for analysis. Once the water inside the sampler was taken, the motor vacuumed the inside of the sampler again so it sucks water until the next sampling.

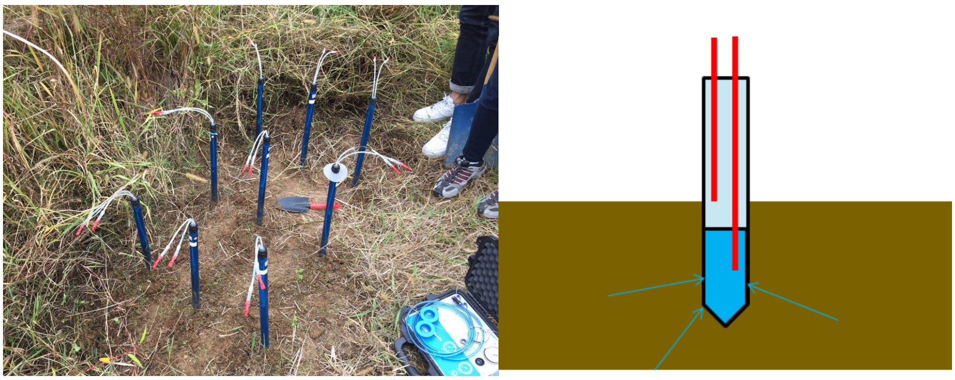


Fig 3.2. Porewater samplers placed in Janghang sampling site to collect direct porewater.

3.1.3 Water monitoring data

Water chemistry data from 12 different stations within Han River in Korea was collected from a website www.koreawqi.go.kr operated by National Institute of Environmental Research, Republic of S.Korea. The site provides instantaneous water quality information from four major river basins in Korea since 2012. Overall there are 70 monitoring stations in S.Korea. Among 23 stations in River Han basin, 12 stations were chosen to consider spatial variability and the stations are: River soyangang, Danyang, River pyeongchang, River Hantan, Dalcheon, Gapyeong, Gangcheon, Gyeongancheon, Guri, Neungseo, Misan, Seosang, which are streams gathering to Han

River.

The current monitoring system automatically measures following environmental factors from each station: pH, dissolved oxygen, electrical conductivity and total organic carbon in common and turbidity, chlorophyll-a, total nitrogen, total phosphorus, NH3-N, NO3-N, PO4-P, VOCs, phenols, heavy metals(Cu, Zn, Pb, Cd) and microorganisms selectively. From the monitoring data on the website, only pH, TOC and temperature were available to be used in this study since the current monitoring system in Korea does not measure ion concentrations other than total-nitrogen and total-phosphorus. The data between June 2014 and October 2016 were collected in this study.

DOC concentrations were calculated from TOC concentrations assumed to be 72% of it. The percentage of DOC in TOC varies greatly depending on characteristics of water and it is known to be in a range of 70-90%. In this study 72% was chosen from a research analyzed characteristics of Nakdong river in S.Korea, one of four river basins(Nakdong River Water Environment Laboratory 2004). The amount of DOC changes significantly depending on the source of pollution. When livestock manure disposal station was in near, the DOC amount increased up to 90% in water.

3.1.4 *Hordeum Vulgare*

In a terrestrial biotic ligand model (TBLM) to predict 50% effective cocentration of copper, which is a concentration inhibiting growth of 50% of the population in species, barley (*hordeum vulgare*) was chosen. Barley has been used widely in toxicity test as it grows fast and is easy to sprout in laboratory. The previous studies about the BLM conducted the experiments with barley to predict heavy metal concentrations inhibiting 50% of its root growth and calculated the BLM parameters determining the binding constant between the heavy metal and the biotic ligand. Additionally barley is sensitive compared to other plants studied in Heemsbergen et al(2009) implying that if the copper concentration in the site were safe enough to protect barley, it would be able to protect other plants in the region.

Table 3.1 Crops grown in field trials of the Australian National Biosolids Research Program with their corresponding geometric means of copper concentrations that inhibited crop yield by 10% (EC10), the lowest observed EC10 and the number of EC10 values for each species (Heemsbergen, 2009).

Crop	Geometric means of EC10 values	Lowest EC10 value	Number of EC10 values
Barley	63.1	30.6	3
Canola	341	88.9	4
Cotton	245	245	1
Maize	175	175	1
Millet	377	377	1
Peanuts	521	406	2
Sorghum	385	385	1
Sugar cane	663	663	1
Triticale	32.4	32.4	1
Wheat	256	156	11

3.1.5 *Daphnia Magna*

In water, *Daphnia Magna* is a good index being used in toxicity test or evaluating the level of contamination. It is a type of cladoceran or water flea commonly found in water system which is very sensitive to the change of environment. In species sensitivity distribution (SSD) which draws a sigmoidal curve indicating the toxic values and the sensitivity to multiple species. When SSD is drawn with cladocerans exposed to copper, *Daphnia magna* is located at the lower part of the curve and it means the species is more sensitive than others in the cladocerans group (Brix et al., 2009). Therefore the BLM parameters for *Daphnia magna* were used in this study to predict an acceptable copper concentration in water to protect aquatic organisms represented by it.

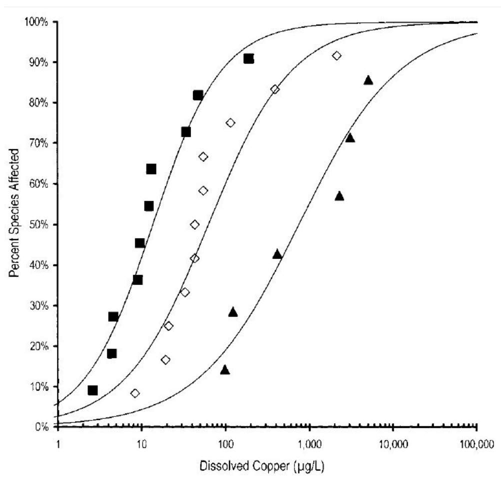


Fig 3.3. Logistic regressions fit to acute toxicity data for cladocerans, cold-water fish, and insects. Cladocerans (■), cold-water fish (◇), and insects (▲) (Brix et al., 2001).

3.2 Method

3.2.1 ICP-OES

Cation concentrations from 10 porewater samples were analyzed by using inductively coupled plasma optical emission spectroscopy (iCAP 7400 ICP-OES, Thermo Fisher Scientific, USA).
In ICP-OES, plasma energy is given to an analysis sample from outside to make the atoms excited. The emission rays or spectrum rays are released when the atoms return to low energy position, and the emission rays that correspond to the photon wavelength are measured.. To generate plasma, first, argon gas is supplied to torch coil, and high frequency electric current is applied to the work coil at the tip of the torch tube. Using the electromagnetic field created in the torch tube by the high frequency current, argon gas is ionized and plasma is generated. This plasma has high electron density and temperature (10000K) and this energy is used in the excitation-emission of the sample. Solution samples are introduced into the plasma in an atomized state through the narrow tube in the center of the torch tube (Hitach High-Technologies).

3.2.2 Visual MINTEQ 3.1

The concentrations of Ca^{2+}, Mg^{2+}, K^{+}, Na^{2+}, pH, DOC and temperature were used as site-specific input variables in Visual MINTEQ 3.1 (Gustafsson, 2013) to calculate activities of cations. The activities were put into equation 5 to find $EA_{50}\{Cu^{2+}\}$ in soil porewater and the BLM-predicted Cu concentration, which is an instantaneous water quality criterion(IWQC) in this study, was the value having the same activity as calculated from equation 5. Visual basic for application(VBA) in excel was used to program a macro to find the IWQC concentration with the $EA_{50}\{Cu^{2+}\}$ activity calculated from the BLM equation. This macro runs Visual MINTEQ 3.1 automatically and uses environmental factors including ion concentrations, pH and DOC with the target $EA_{50}\{Cu^{2+}\}$ value. Then the macro repeats by increasing the copper concentration until it finds the copper concentration having the target activity within 5% of error. It assumed CO_2 is at equilibrium between soil porewater and air and the CO_2 pressure (P_{CO2}) was set at 0.00038 atm. This total concentration of copper under the specific environmental factors as input variables is used as the IWQC value to apply the FMB.

In river monitoring system, only pH, DOC and temperature were available from the current database. The amount of calcium present in water was assumed to be 16mg/L as world average river water has a average concentration of Ca^{2+} 0.367mM (Berner 1987). Visual MINTEQ 3.1 were run with pH, DOC, temperature and the assumed calcium concentration, which is the fixed amount of Ca^{2+} for each monitoring station to calculate Ca^{2+} and CO_3^{2-} activities, as input variables. The CO_2 was assumed to be at equilibrium between water and air and its pressure was set at 0.00038 atm. Using the equation 7, 50% effective activity $EA_{50}\{Cu^{2+}\}$ was calculated and with the macro in excel, the IWQC for Cu concentration having the same copper activity from the BLM calculation was found.

4. Results and discussion

4.1 Soil porewater

4.1.1 Porewater data in time series

During the 5 months of sampling period, 10 soil porewater samples were collected from Janghang site located in Chungcheongnamdo province in S.Korea. Cation concentrations (Ca^{2+}, Mag^{2+}, Na^{+} and K^{+}), pH and DOC were measured for each sample and the results are indicated in Table4.1. Each concentration changed continuously over the sampling period resulting in different 50% effective concentration(EC50) of copper to barley (*Hordeum Vulgare*).

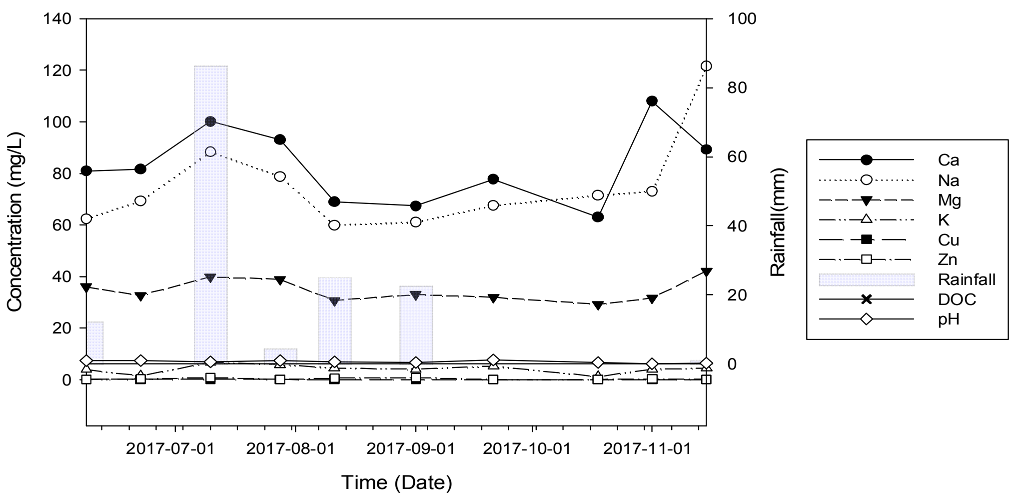


Fig 4.1. Change of ion concentrations, dissolved organic carbon, pH and rainfall during the sampling period.

4.1.2 Application of BLM

Thakali et al.(2006a) developed the TBLM to predict ecotoxicity of Cu in soil porewater and evaluate the effect of cations Ca^{2+}, Mg^{2+}, Na^{+}, K^{+} and H^{+} on Cu complexation and speciation in solution when tested for barley root elongation test. Ca^{2+}, Mg^{2+}, Na^{+} and K^{+} did not have significant competing effect with free Cu^{2+} ion for the BL site whereas H^{+} worked as a competing cation and yielded the binding constant with the BL site $\log K_{HBL}=6.48$ (1). Thus, the effects of four cations were excluded when calculating the free copper ion activity from equation 5. Only the activity of H^{+} ion, which is pH, was used as an input parameter to find the copper activity. To find a copper concentration having the same activity as calculated using BLM, the excel macro was run until it found the target copper activity within 5% of error. These copper concentrations are 50% effective concentration (EC50) which influence 50% of *horadeum vulgare* when exposed in Janghang site. They were listed in the Table 4.2 as IWQC meaning the predicted copper concentration.

Table 4.1. Porewater chemistry information sampled from Janghang heavy metal contaminated area from June 8th to November 15th 2017 analyzed by ICP-OES

Location	Date	Rainfall (mm)	pH	Toxic Unit	Temperature (℃)	DOC (mg/L)	Cu (mg/L)	Zn (mg/L)	Ca (mg/L)	K (mg/L)	Mg (mg/L)	Na (mg/L)
Janghang	2017-06-08	12.3	7.45	0.57	25	12.90	0.082	0.052	80.97	3.895	35.94	62.39
	2017-06-22	0.00	7.29	0.82	26	4.25	0.100	0.205	81.60	1.400	32.68	69.31
	2017-07-10	86.4	7.00	1.28	28	11.15	0.102	0.745	100.12	6.710	39.76	88.33
	2017-07-28	4.40	7.32	0.59	30	9.88	0.057	0.114	92.98	5.791	38.85	78.79
	2017-08-11	25.1	6.87	0.58	30	6.74	0.026	0.531	68.96	4.436	30.66	59.86
	2017-09-01	22.6	6.68	1.31	28	5.42	0.041	0.767	67.39	4.104	32.94	61.06
	2017-09-21	0.00	7.54	0.29	24	5.37	0.019	0.008	77.74	5.205	31.88	67.55
	2017-10-18	0.00	6.58	0.38	19	4.8	0.010	0.042	62.99	1.099	29.19	71.46
	2017-11-01	0.00	6.21	0.74	16	4.52	0.016	0.270	107.99	4.035	31.60	73.07
	2017-11-15	1.10	6.27	0.51	13	5.65	0.014	0.129	89.24	4.360	42.08	121.50

Table 4.2. BLM-predicted 50% effective concentration (EC50), the dissolved copper concentration in porewater and FMB parameters.

Location	Date	EA50{Cu^{2+}}	IWQC (μg/L)	Cu (μg/L)	Toxic Unit	$Cu_{i,cop}$ (μg/L)	$TU_{i,comp}$
Janghang	2017-06-08	2.267E-09	143.2	82.2	0.57	31.2	0.218
	2017-06-22	2.365E-09	122.4	100	0.82	38.0	0.311
	2017-07-10	2.666E-09	80.0	102	1.28	38.8	0.485
	2017-07-28	2.344E-09	96.0	56.6	0.59	21.5	0.224
	2017-08-11	2.882E-09	44.7	26.1	0.58	9.90	0.222
	2017-09-01	3.340E-09	31.5	41.2	1.31	15.7	0.498
	2017-09-21	2.226E-09	66.4	19.0	0.29	7.20	0.109
	2017-10-18	3.674E-09	27.2	10.3	0.38	3.90	0.144
	2017-11-01	5.860E-09	21.8	16.2	0.74	6.20	0.283
	2017-11-15	5.368E-09	27.3	14.0	0.51	5.30	0.195

4.1.3 Calculation of FMB

The current copper concentrations in the site were less than the BLM-predicted EC50 or instantaneous water quality criteria (IWQC) most of the time during the sampling period but on the 3rd and 6th sampling, the copper concentration in porewater exceeded IWQC. This implies the dissolved copper concentrations in Janghang porewater could be hazardous to local plants in the area inhibiting their growth time to time. To evaluate how often the dissolved copper concentrations are in compliance with the IWQC concentrations predicted by BLM, toxic unit was calculated by dividing the dissolved copper concentration by the IWQC concentration for each sample. TU=1 means they are at the same concentration, when TU is less than 1 the dissolved copper concentrations are less than the IWQC concentrations or in other words they do not exceed the BLM-predicted safe concentrations. If TU is greater than 1, the copper concentrations in the site porewater exceed the BLM predictions and may affect barley or a few local plants in the area. The dissolved copper concentrations, the IWQC concentrations and the toxic units for each sample are plotted together in time series in order to check their time variability during the sampling period. Because the dissolved copper concentrations are less than the IWQC concentrations for 8 samples, toxic units are less than 1 except in July 10th and September 1st. Then the time series plot is transformed to a cumulative probability plot arranging the sampling data from the least to the most occurrence. In order to evaluate the compliance of the copper concentration in Janghang porewater, the target exceedance frequency is set to be once in three years. This means that the site has a 1-in-3 year allowance with copper concentration and regulates the dissolved copper concentration not to exceed the BLM-predicted IWQC concentration more often than once in three years. In probability, this is 1day/1095days yielding 0.000913 which is equivalent to say that the probability of complying the IWQC concentrations in this site water should be 99.91%. Toxic unit value in the cumulative probability plot at 99.91% is denoted as TU_{EF} and this value can be calculated using equation 9. TU_{EF} tells whether the dissolved copper concentration exceeds the IWQC concentration based on the once in three year frequency during the sampling period. If it is greater than 1, the dissolved copper concentration is greater than the IWQC concentration more frequent than it is supposed to be, so the copper concentration in site water should decrease to protect the local organisms. In Janghang porewater, TU_{EF} is 4.xxx predicting that the dissolved copper concentrations would exceed the BLM-predicted IWQC concentrations more often than the target exceedance frequency of once in three years and therefore the current dissolved copper concentration should decrease to be safe enough to protect barley and a few local plants in the area. To determine by how much it should decrease, the adjustment factor is calculated as the inverse of TUEF, which decreases the previous TU_{EF} value to 1 meaning that the maximum copper concentration in porewater should be no greater than the IWQC concentration. The maximum TU_{EF} with a new distribution is became 1, and the dissolved copper concentration also decreased by TU distribution decreased. The new dissolved copper concentration is calculated by multiplying the previous copper concentration and the adjustment factor and denoted as $Cu_{i,comp}$ meaning the copper concentration in compliance with the

IWQC concentrations. Thus the site-specific copper criterion should be in the range of $Cu_{i,comp}$ and it would be the highest concentration in the distribution, which is at 99.91% in the cumulative probability plot. In Janghang porewater, the highest concentration of dissolved copper that could reach is 0.17mg/L to comply the BLM-predicted IWQC concentrations to protect barley and the plants in the area. When the dissolved copper concentration goes higher than 0.17mg/L, it would reveal toxic effects inhibiting their growth.

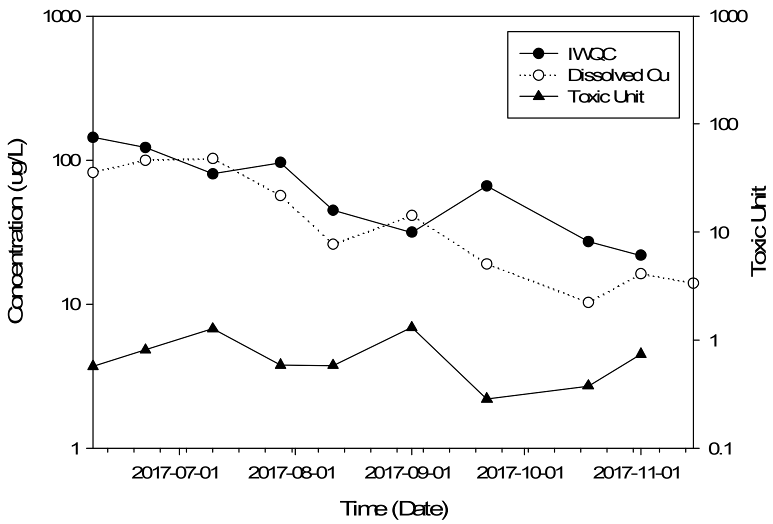


Fig 4.2. BLM-predicted instantaneous water quality criteria (IWQC), in-stream Cu concentrations (Dissolved Cu), and toxic units plottes as a time series.

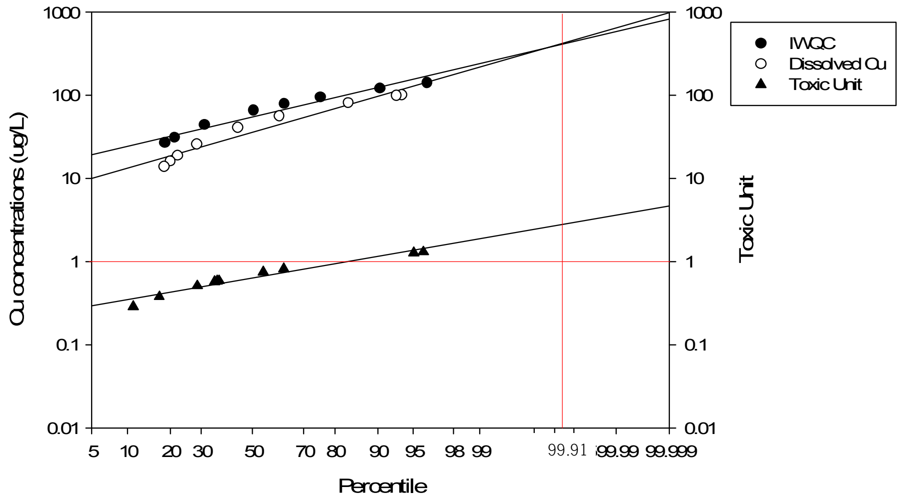


Fig 4.3. BLM-predicted instantaneous water quality criteria (IWQC), in-stream Cu concentrations (Dissolved Cu), and toxic units plotted in a cumulative probability distributions indicating that TU at exceedance frequency (99.91%) exceeds 1.

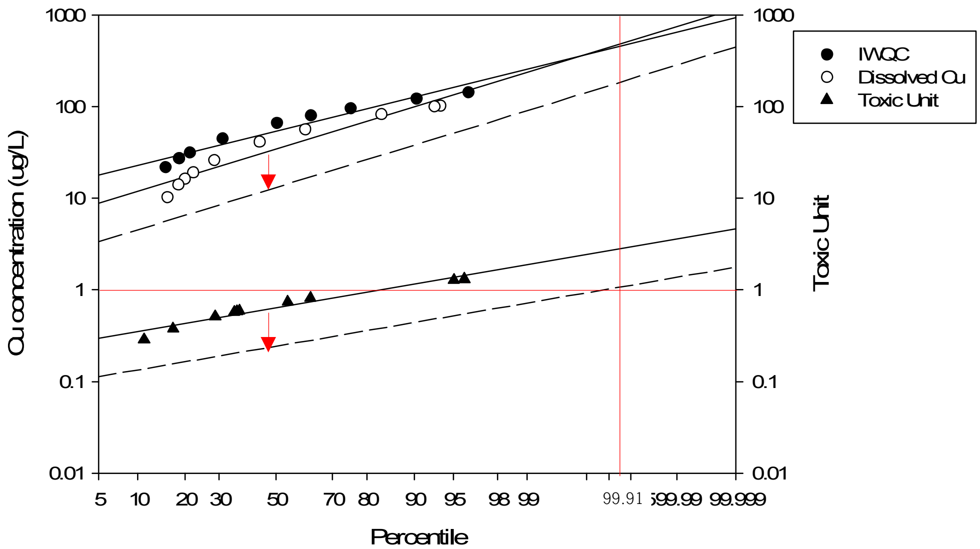


Fig 4.4. BLM-predicted instantaneous water quality criteria (IWQC), in-stream Cu concentrations (Dissolved Cu), and toxic units plotted in a cumulative probability distributions with solid lines and the dashed lines represent revised distributions of Dissolved Cu and Toxic Unit meeting the exceedance frequency.

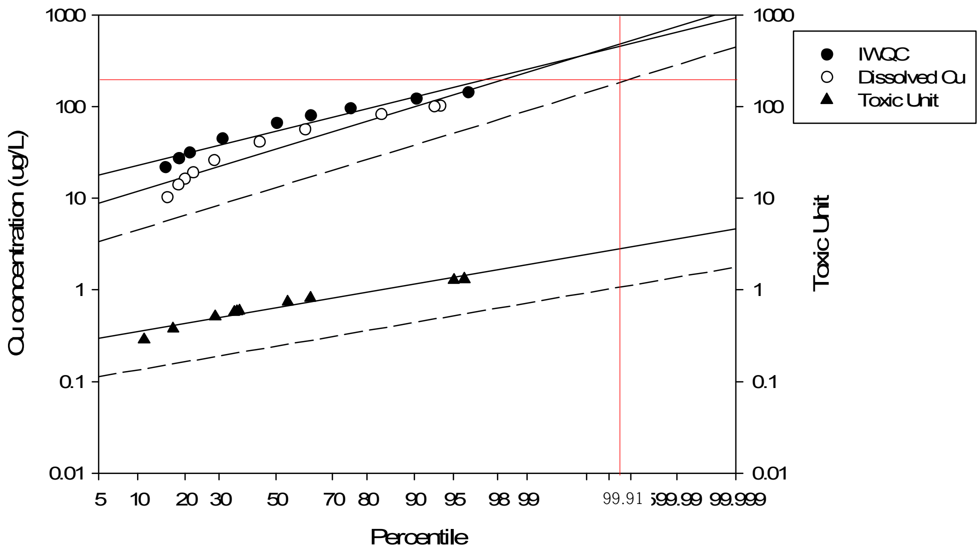


Fig 4.5. BLM-predicted instantaneous water quality criteria (IWQC), in-stream Cu concentrations (Dissolved Cu), and toxic units plotted in a cumulative probability distributions with solid lines and the fixed monitoring benchmark is the Cu concentration where the dashed line of Dissolved Cu meets exceedance frequency (99.91%).

The FMB value is a ecotoxicological heavy metal criterion in specific site to protect the living organisms and thus it is not comparable with the previous criterion currently being used S.Korea. Hazardous concentration of copper protecting 95% of species in soil is calculated to be in a range of 0.04 - 10 mg/L with general Kd values in soil in a range of 1.4 - 333 L/kg at pH 4.5 - 9.0. In domestic soil, it is calculated as 0.64 mg/L. The regulation of copper concentration in drinking water is 1 mg/L.

The FMB value of 0.17 mg/L at this specific Janghang site implies that the copper concentration should be regulated to be less than this number. The current dissolved copper concentrations in the site were mostly less than the BLM-predicted IWQC concentrations except at two points and in a cumulative probability plot it showed that with the current tendency of the dissolved copper concentration, it may exceed the IWQC more frequently than the target exceedance frequency, once in three years. Therefore this final FMB is the highest number that the dissolved copper concentration in this site could reach possibly by being in compliance with the IWQC concentrations. 0.17 mg/L is lower than the hazardous concentration of 0.04 – 10 mg/L or 0.64 mg/L in Korean soil that protects 95% of the total species in soil which is calculated. The FMB and the HC5 are not comparable as they were calculated with different purpose and method but the study confirmed that the FMB from Janghang site is within the range of HC5.

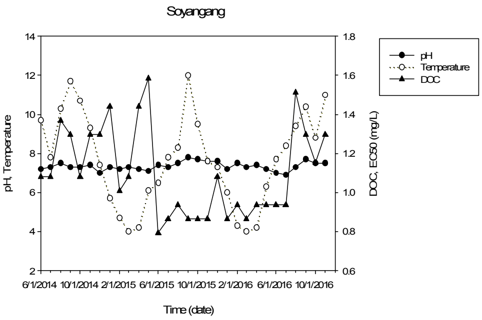
Table 4.3. Copper criterion in 5% hazardous concentration (HC5), fixed monitoring benchmarks (FMB) and groundwater.

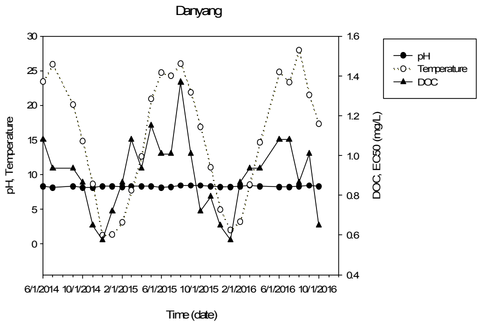
Criterion	Value (mg/L)	Application
HC5	0.04 – 10 (Domestic soil: 0.64)	In soil
FMB	0.17	In soil porewater
Groundwater	1	Drinking water

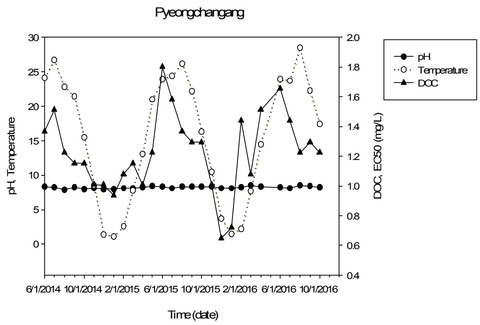
4.2 Stream water

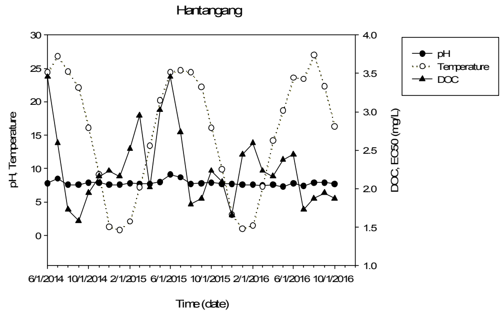
4.2.1 Stream water data in time series

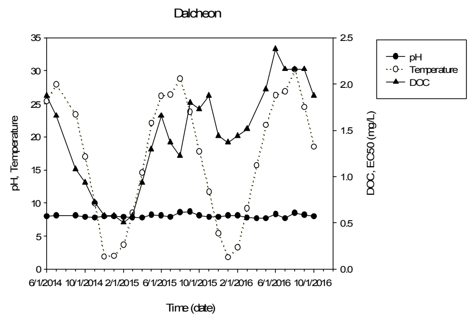
In stream water environmental factors such as pH, DOC and temperature vary greatly and that would result in a change of BLM predictions over time. In Han River basin in S.Korea, 12 monitoring stations were chosen to observe time variability in each factor from June 2014 to October 2016.

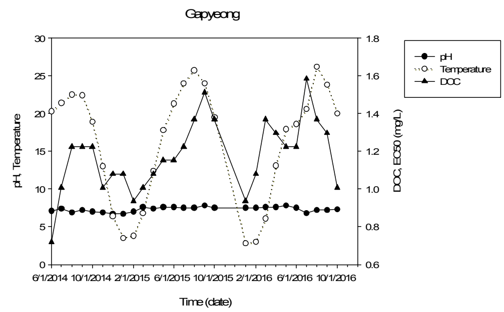

Soyangang
pH, Temperature
DOC, EC50 (mg/L)
Time (date)
pH
Temperature
DOC

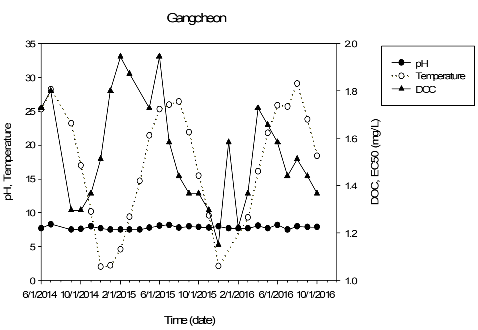

Danyang
pH, Temperature
DOC, EC50 (mg/L)
Time (date)
pH
Temperature
DOC

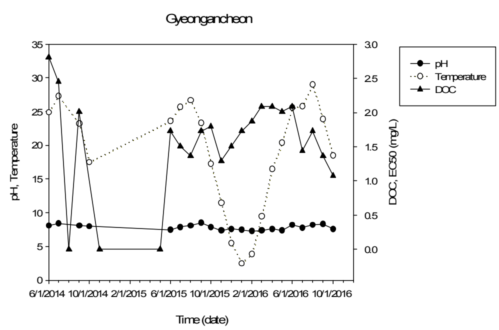

Pyeongchangang
pH, Temperature
DOC, EC50 (mg/L)
Time (date)
pH
Temperature
DOC


Hantangang
pH, Temperature
DOC, EC50 (mg/L)
Time (date)
pH
Temperature
DOC


Dalcheon
pH, Temperature
DOC, EC50 (mg/L)
Time (date)
pH
Temperature
DOC


Gapyeong
pH, Temperature
DOC, EC50 (mg/L)
Time (date)
pH
Temperature
DOC


Gangcheon
pH, Temperature
DOC, EC50 (mg/L)
Time (date)
pH
Temperature
DOC


Gyeongancheon
pH, Temperature
DOC, EC50 (mg/L)
Time (date)
pH
Temperature
DOC

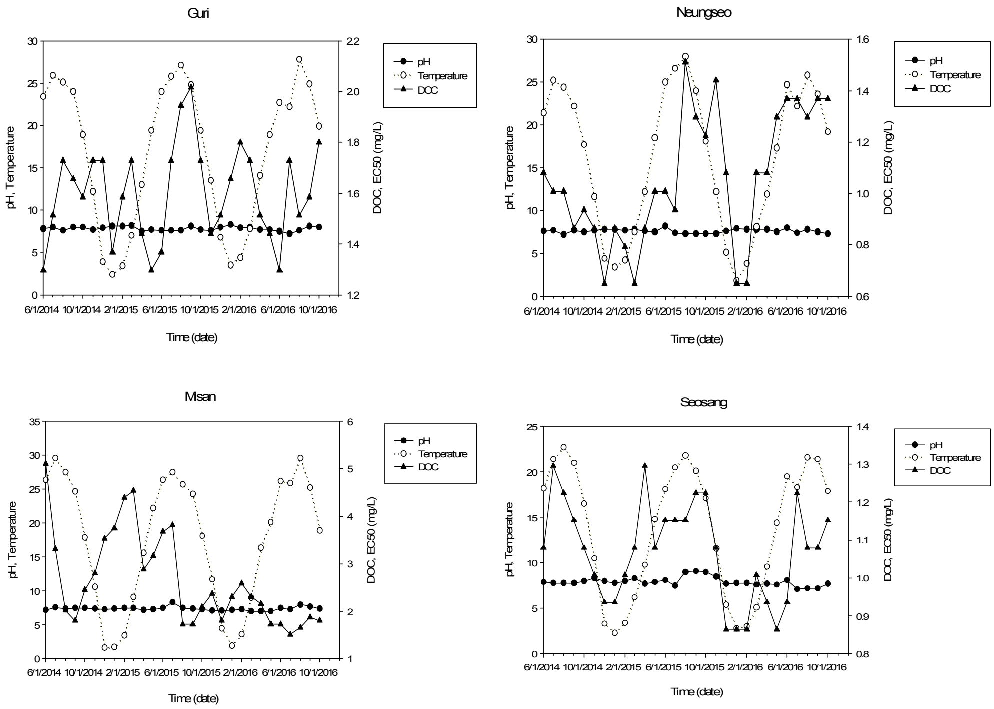


Fig 4.6. The change of pH, temperature and dissolved organic carbon in 12 different monitoring stations.

Table 4.4. The water quality monitoring data obtained from Danyang monitoring station within Han River.

Station	Date	pH	$EC_{50}\{Cu^{2+}\}$ (mol/L)	IWQC (µg/L)	Cu (µg/L)	$\{CO_3^{2-}\}$	DOC (mg/L)	Temperature (℃)
Danyang	May-14	8.3	2.81E-09	57.7	2.00	1.03.E-05	1.3	19
	Jun-14	8.3	2.75E-09	51.0	2.00	1.06.E-05	1.1	23.4
	Jul-14	8.1	4.99E-09	41.5	2.00	4.29.E-06	0.9	25.9
	Aug-14	NR[a]	NR[a]	NR[a]	2.00	NR[a]	NR[a]	NR[a]
	Sep-14	8.3	2.80E-09	44.0	2.00	1.04.E-05	0.9	20.1
	Oct-14	8.1	5.22E-09	40.7	2.00	3.89.E-06	0.9	14.8
	Nov-14	8.1	5.43E-09	29.8	2.00	3.53.E-06	0.6	8.6
	Dec-14	8.3	3.36E-09	32.5	2.00	7.55.E-06	0.6	1.2
	Jan-15	8.3	3.36E-09	36.2	2.00	7.56.E-06	0.7	1.3
	Feb-15	8.2	4.40E-09	42.1	2.00	4.99.E-06	0.9	3.1
	Mar-15	8.3	3.10E-09	50.7	2.00	8.72.E-06	1.1	7.7
	Apr-15	8.3	2.95E-09	43.6	2.00	9.48.E-06	0.9	12.6
	May-15	8.3	2.78E-09	54.3	2.00	1.04.E-05	1.2	20.9
	Jun-15	8.1	5.01E-09	45.0	2.00	4.27.E-06	1.0	24.7
	Jul-15	8.2	3.78E-09	46.4	2.00	6.75.E-06	1.0	24.3
	Aug-15	8.4	1.92E-09	NR[a]	2.00	1.71.E-05	1.4	26
	Sep-15	8.4	1.95E-09	48.4	2.00	1.67.E-05	1.0	21.9
	Oct-15	8.4	2.02E-09	38.0	2.00	1.59.E-05	0.7	16.9
	Nov-15	8.3	3.00E-09	40.0	2.00	9.25.E-06	0.8	11
	Dec-15	8.2	4.31E-09	31.2	2.00	5.20.E-06	0.6	4.9
	Jan-16	8.2	4.45E-09	31.0	2.00	4.86.E-06	0.6	2
	Feb-16	8.3	3.27E-09	43.5	2.00	7.93.E-06	0.9	3.2
	Mar-16	8.4	2.20E-09	44.7	2.00	1.40.E-05	0.9	8.5
	Apr-16	8.3	2.90E-09	43.6	2.00	9.75.E-06	0.9	14.6
	May-16	NR[a]	NR[a]	NR[a]	NR[a]	NR[a]	NR[a]	NR[a]
	Jun-16	8.2	3.77E-09	50.0	2.00	6.77.E-06	1.1	24.8
	Jul-16	8.2	3.79E-09	49.8	2.00	6.70.E-06	1.1	23.3
	Aug-16	8.3	2.71E-09	44.5	2.00	1.09.E-05	0.9	28
	Sep-16	8.4	1.96E-09	48.4	2.00	1.66.E-05	1.0	21.5
	Oct-16	8.3	2.85E-09	33.2	2.00	1.01.E-05	0.6	17.3

[a] NR = not reported.

4.2.2 Modified BLM application

The pH was in a range of 6 to 8 but in the most of the stations it exceeded 7.0 and thus the modified BLM equation by Want et al.(2012) was used to predict the copper toxicity in stream water because it takes into accounts for copper speciation such as CuOH and $CuCO_3$ in higher pH assuming not only free copper ions but also these complexes also have toxic effects to the aquatic organisms. Temperature variation had a smiliar pattern in each station decreasing rapidly in winter and increasing up to 30℃ in summer in overall. To apply the BLM, there were major assumptions in this study: dissolved copper concentration was set to 2 μg/L in each monitoring system with relative standard deviation of 0.6 and hardness was given as 40 mg/L $CaCO_3$. This was because of lack of information provided by the current river monitoring system in S.Korea. Heavy metals (Cu, Pb, Zn, Ni, As) and hardness are not being measured at 12 selected monitoring system here as it is not enforced by Korean law. Copper concentration was assumed to be 2 μg/L because it is a detection limit for copper at monitoring stations in mountain areas where the copper concentrations were found to be between 0 and 2 μg/L. The amount of calcium was assumed as 16 mg/L from world rivers (Berner 1987). With these environmental factors in each monitoring station as input variables, Visual MINTEQ 3.1 was run to calculate activities of Ca^{2+} and CO_3^{2-} to be applied in the BLM and calculate the 50% effective activity of free copper ion influencing *Daphnia magna* in water. The results of calculation is listed in a Table 4.7.

Table 4.5. The BLM-predicted copper concentration $[Cu]_T$, dissolved copper concentration and FMB parameters in Danyang monitoring station.

Station	Date	IWQC (μg/L)	Cu (μg/L)	Toxic Unit	$Cu_{i,comp}$	$TU_{i,comp}$
Danyang	May-14	57.70	2.00	0.035	25.06	0.434
	Jun-14	51.00	2.00	0.039	25.06	0.491
	Jul-14	41.50	2.00	0.048	25.06	0.604
	Aug-14	NR[a]	2.00	NR[a]	NR[a]	NR[a]
	Sep-14	44.00	2.00	0.045	25.06	0.570
	Oct-14	40.70	2.00	0.049	25.06	0.616
	Nov-14	29.80	2.00	0.067	25.06	0.841
	Dec-14	32.50	2.00	0.062	25.06	0.771
	Jan-15	36.20	2.00	0.055	25.06	0.692
	Feb-15	42.10	2.00	0.048	25.06	0.595
	Mar-15	50.70	2.00	0.039	25.06	0.494
	Apr-15	43.60	2.00	0.046	25.06	0.575
	May-15	54.30	2.00	0.037	25.06	0.462
	Jun-15	45.00	2.00	0.044	25.06	0.557
	Jul-15	46.40	2.00	0.043	25.06	0.540
	Aug-15	NR[a]	2.00	NR[a]	25.06	NR[a]
	Sep-15	48.40	2.00	0.041	25.06	0.518
	Oct-15	38.00	2.00	0.053	25.06	0.660
	Nov-15	40.00	2.00	0.050	25.06	0.627
	Dec-15	31.20	2.00	0.064	25.06	0.803
	Jan-16	31.00	2.00	0.065	25.06	0.808
	Feb-16	43.50	2.00	0.046	25.06	0.576
	Mar-16	44.70	2.00	0.045	25.06	0.561
	Apr-16	43.60	2.00	0.046	25.06	0.575
	May-16	NR[a]	NR[a]	NR[a]	NR[a]	NR[a]
	Jun-16	50.00	2.00	0.040	25.06	0.501
	Jul-16	49.80	2.00	0.040	25.06	0.503
	Aug-16	44.50	2.00	0.045	25.06	0.563
	Sep-16	48.40	2.00	0.041	25.06	0.518
	Oct-16	33.20	2.00	0.060	25.06	0.755

[a] NR = not reported.

When the activities were calculated, 50% effective concentrations or IWQC for each sample were found which had the same activities as calculated from the BLM. The IWQC concentrations were calculated greater than the dissolved copper concentration because it was set to be the detection limit which is a very small number.

4.2.3 Finding FMB values

When applying the concept of FMB, the dissolved copper concentration is far less than the IWQC concentrations and that results in too small TU_{EF} value considering the once in three year exceedance frequency. This implies that the dissolved copper concentrations are too small compared to the IWQC concentrations if it is at 2 μg/L and thus it is allowed to be increased unless it exceeds the IWQC. The current dissolved copper concentrations would be lifted upward by the amount of current TU_{EF} becoming 1 and form a new dissolved copper distribution in compliance with the IWQC or denoted as $Cu_{i,comp}$. The FMB value is the highest concentration within the new copper concentration distribution that will not exceed the IWQC more frequently than once in three years. FMB values vary from 2.63 to 7.41 μg/L in 12 monitoring stations within Han River basin yielding up to 95% difference between each station. This is because of different pH, DOC and temperature in different stations and varying IWQC concentrations from them.

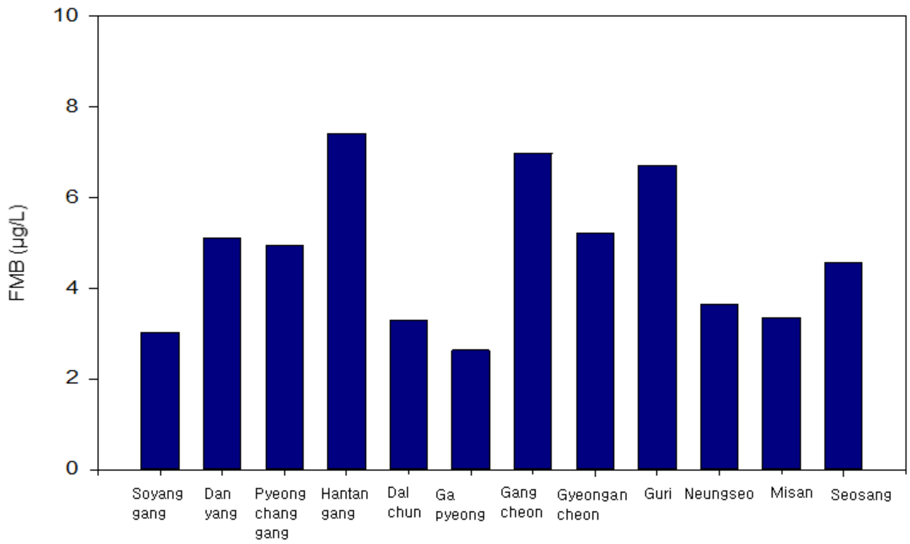


Fig 4.7. The difference of predicted FMB values in each monitoring station.

4.2.4 Comparison with various copper criteria

5% hazardous concentration (HC5) and 50% hazardous concentration (HC50) of copper calculated in Korean water system which protect 5% and 50% of species are 1.14 μg/L and 81.5 μg/L respectively. The species sensitivity distribution (SSD) in Figure 4.8 was generated from the toxicity data for 174 species in water through ECOTOX database by USEPA.

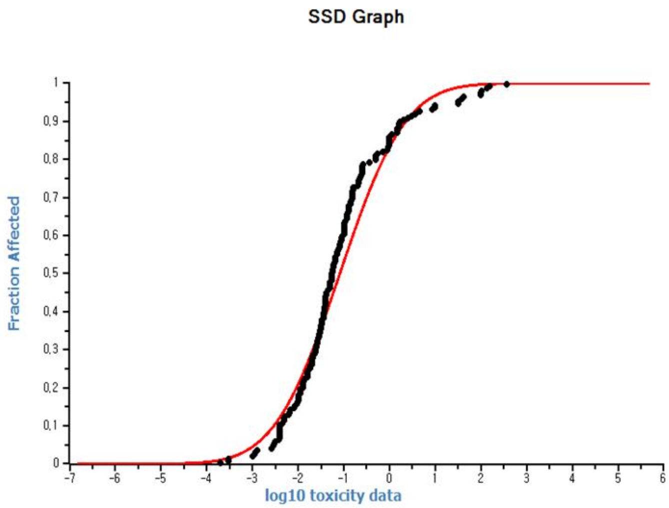


Fig 4.8. Species sensitivity distribution (SSD) for 174 species found in water system and their sensitivity to copper.

Various ecological copper criterion in water in different nations are listed in Table 4.6.

Table 4.6. National criterion for copper determined ecologically in water.

National criterion			Value (μg/L)
S.Korea			-[1]
USA (USEPA)	R3 BTAG[2]		9
	R6[3]		7
	R5 ESLs[6]	Surface Water Screening Benchmark	1.58
	R4[7]	Acute	9.22
		Chronic	6.54
	NAWQC[8]	Acute	13
		Chronic	9
	LCV Aquatic Plants[9]		1
	LCV Daphnids[10]		0.23
	LCV Fish[11]		3.8
	LCV Non-Daphnid Inverts[12]		6.07
	OSWER[13]		11
	EC20 Daphnids[14]		0.205
	EC20 Fish[14]		5
	EC20 Sensitive Species[14]		0.26
	EC25 Bass Population[14]		8.6
Canada	CCME WQE$_E$[15]		2
Netherlands	IV[4]		75
	TV[5]	<10 m	15
		>10 m	1.3

1. Not available.
2. Biological Technical Assistance Group Freshwater Screening Benchmarks suggested by USEPA's Region 3.
3. Surface Water Screening value suggested by USEPA's Region 6.
4. Intervention Value of the Dutch National Institute for Public and the Environment.
5. Target Value of the Dutch National Institute for Public and the Environment.
6. Ecological Screening Levels (ESLs) suggested by USEPA's Region 5.
7. Surface Water Screening Benchmark suggested by USEPA's Region 4.
8. Surface Water Screening Benchmark suggested by National Ambient Water Quality Criteria.
9. Surface Water Screening Benchmark derived by the lowest acceptable chronic value for aquatic plants is based on the geometric mean of the Lowest Observed Effect Concentration and the No Observed Effect Concentration.
10. Surface Water Screening Benchmark derived by the lowest acceptable

chronic value for daphnids is based on either the geometric mean of the Lowest Observed Effect Concentration and the No Observed Effect Concentration or an extrapolation from 48-hour LC50s using equations from Suter et al (1987) and Suter (1993).
11. Surface Water Screening Benchmark derived by the lowest acceptable chronic value for fish is based on either the geometric mean of the Lowest Observed Effect Concentration and the No Observed Effect Concentration or an extrapolation from 96-hour LC50s using equations from Suter et al (1987) and Suter (1993).
12. Surface Water Screening Benchmark derived by the lowest acceptable chronic value for Non-Daphnid Inverts is based on the geometric mean of the Lowest Observed Effect Concentration and the No Observed Effect Concentration.
13. Ambient Water Quality Criteria from OSWER (1996).
14. Surface Water Screening Benchmark.
15. Environmental Water Quality Guideline of Canadian Council for Ministry of the Environment.

The values of ecological copper criteria vary from 0.205 to 75 μg/L based on standard and method used by different countries and the FMB results from 12 monitoring stations within Han River in Korea are placed in the worldwide range.

4.2.5 Importance of measuring calcium

Because the current water monitoring system in Korea does not measure cation concentrations and heavy metal concentrations in most of stations, these two factors were assumed in this study. In order to check the effect of Ca^{2+} in FMB values, the concentration of Ca^{2+} differed from 0 to 2 mM. When Ca^{2+} was 0 mM meaning none present in the solution, the EC50 or FMB value was the highest then it decreased dramatically if Ca^{2+} increased to 0.4 mM. Unlike the BLM assumption that cations cause competing effects with free heavy metal ions for the biotic ligand site and reduce toxic effects, the result indicated the copper toxicity increased when Ca^{2+} was added from zero to 0.4 mM. This is because the amount of free copper ions in solution increased when Ca^{2+} is newly added to the solution. Free copper ions formed complexes with DOC at first and when Ca^{2+} ions were introduced they replaced free copper ions from the DOC complexes. Then the amount of the free copper ions in solution increase compared to the circumstance where Ca^{2+} were not present. When Ca^{2+} concentration increases from 0.4 to 2 mM, EC50 increases slowly indicating less toxicity than before. This is because of competing effects between free copper ions and Ca^{2+} ions in solution as the BLM assumes. The FMB with Ca^{2+} 0 mM is 28 μg/L which is 7 times greater than the FMB value of 3.999 μg/L with Ca^{2+} 2 mM. Therefore the measurement of Ca is essential to predict copper criterion in site water more accurately. Furthermore the concentration of calcium in water affects the change in FMB values greater than other cations (Mg^{2+}, Na^{+} and K^{+}) and anions (Cl^{-}, SO_4^{2-} and NO_3^{-}). While other ions changed the FMB values within 1% of difference, the change of Ca concentration from 0 to 10 mM varied the FMB concentration from 0.08 to 0.13 μg/L. This indicates that the calculation of the FMB concentration is very sensitive to the dissolved Ca concentration.

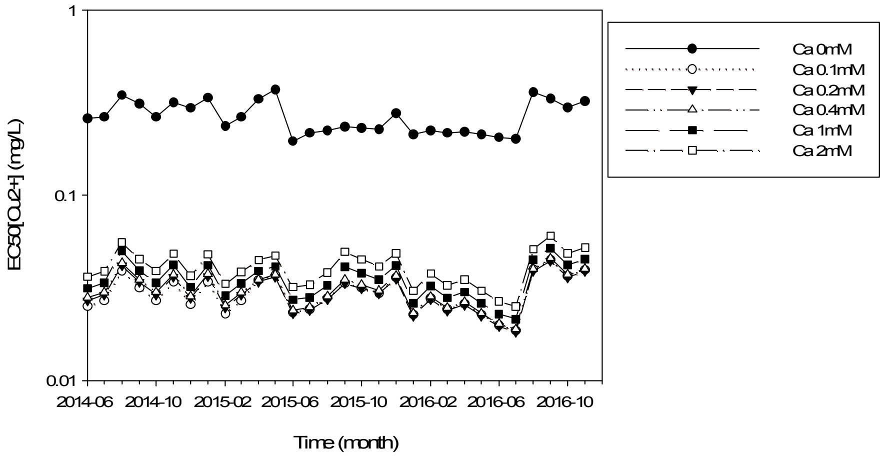


Fig 4.9. Distributions of BLM-predicted 50% effective concentration (EC50) of copper with different amount of Ca^{2+} ions.

Table 4.7. The change of EC50 and FMB values when the amount of Ca^{2+} ions in solution changes.

	Ca 0mM	Ca 0.4mM	Ca 1mM	Ca 2mM
EC50[Cu] (mg/L)	0.268	0.031	0.036	0.041
FMB (μg/L)	28.87	3.017	3.406	3.999

4.2.6 Importance of measuring copper

Heavy metal ions are also not measured monitoring stations in general. As the concept of FMB is a comparison between the actual Cu concentration in site water and the BLM-predicted IWQC concentrations, the dissolved copper concentration is an important factor calculating the FMB value in the region. To evaluate the role of actual copper concentrations, its distribution was differed with different standard deviations. The average of the distributions remained constant as 2 μg/L as set in the assumption, but the standard deviation changed from 1 to 1.5 to compare the FMB values resulted from it. When the standard deviation was assumed as 1, the predicted FMB is 4.30 μg/L and it increases when the standard deviation increases. The FMB values increase as 8.32 μg/L, 11.4 μg/L, 15.3 μg/L, 17.4 μg/L and 23.7 μg/L respectively when the standard deviations are 1.1, 1.2, 1.3, 1.4 and 1.5. The predicted FMB in water varies greatly depending on the dissolved copper concentration in solution.

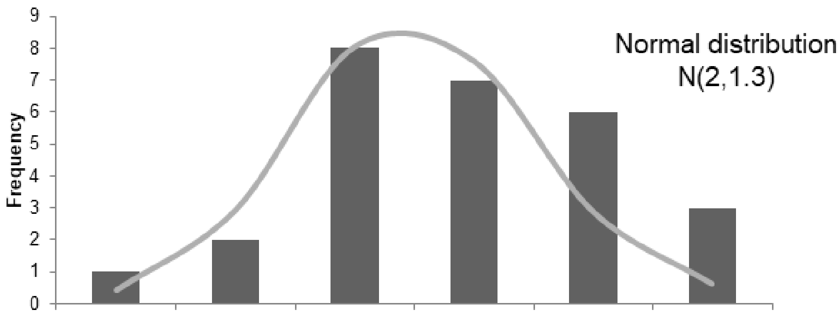


Fig 4.10. The assumed copper distribution when predicting the FMB values in the monitoring stations.

Table 4.8. The change of FMB values when the standard deviation of the copper distribution differs.

σ^2	1.0	1.1	1.2	1.3	1.4	1.5
FMB (μg/L)	4.30	8.32	11.4	15.3	17.4	23.7

5. Conclusions

In this study, the necessity of a new method providing a copper concentration criterion to protect local organisms ecotoxicologically was introduced by applying the fixed monitoring benchmarks (FMB). The study was conducted to use FMB in soil porewater and Han River in S.Korea. Its application in soil porewater was done at one specific sampling site in Janghang, Chungcheongnamdo provice in S.Korea. In order to obtain spatially different FMB values, 12 different monitoring stations in Han River were chosen.

(1) Previous prediction models including the biotic ligand model do not take temporal variability into account and that resulted in different criterion concentrations when measured. To find a single copper criterion which protects local organisms in the area eocotoxicologically, it is necessary to incorporate the BLM prediction of copper toxicity and the time variability of environmental factors at the site.

(2) The FMB is a probability based method combining the BLM and the actual heavy metal concentration at site water. Its application in soil porewater provides a copper concentration of 0.17 mg/L of Janghang site to protect barley and the plants in the region.

(3) In river system, spatial differences of copper concentrations up to 95% between 12 monitoring stations were predicted because of different pH, DOC and temperature in each station.

(4) To make the predictions in river system more accurate and provide an ecotoxicological copper criterion, it is important to measure the actual copper concentrations and cations' concentrations on regular basis through the monitoring system. The current monitoring system does not consider cations and DOC as contaminants and therefore do not measure them but they may influence copper toxicity by forming organic matter complexes or having competition effects with free copper ions. The copper toxicity varies greatly depending on the presence of calcium and thus the amount of calcium should be monitored with the copper concentration in stream water. In addition the concentration of dissolved copper plays an important role determining the site-specific acceptable copper criterion using the fixed monitoring benchmarks as it predicts the concentration based on the current distribution of the copper ion. For this reason, the copper concentration in stream water should be measured as well.

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초록

수계에서의 현장 특이적 구리 허용농도 결정을 위한 fixed monitoring benchmarks와 독성영향인자 시계열 데이터 활용 기법에 관한 연구

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Biotic ligand model (BLM)은 수계 내 환경 인자들을 반영하여 50% 생물종에 영향을 미치는 생태 독성학적 구리의 농도(50% effective concentration, EC50)를 예측하기 위해 개발된 모델로 2000년대 이후 널리 쓰이고 있다. 하지만 BLM 예측값을 결정하는 pH, DOC, 이온 농도와 같은 환경 인자들이 시간에 따라 변화하게 되고 따라서 BLM으로 산출 된 구리의 예측 농도 역시 변화하기 때문에 한 모니터링 지점에서 기준이 되는 중금속의 농도를 산정하기 힘들다는 한계가 있다. 이를 보완하기 위해 fixed monitoring benchmarks (FMB) 라는 기법이 제안된 바 있다. FMB는 실제 구리 농도가 BLM으로 예측된 구리의 농도를 얼마나 준수하는지를 평가하고 BLM의 예측 값을 준수하는 범위 내에서 해당 수계에 존재 가능한 가장 높은 구리의 농도를 확률적으로 계산한다.

본 연구에서는 FMB를 토양 공극수에 적용하기 위해 5개월간 충청남도 서천군 장항읍에서 공극수를 샘플링 하여 pH, DOC, 양이온 농도를 측정하였으며 시간에 따라 측정 값들이 변화함을 확인 하였다. 공극수의 특성이 변화하기 때문에 BLM으로 예측한 구리의 농도 역시 변화하였고

공극수에 존재하는 구리의 농도가 샘플링 기간 동안 예측 값을 2회 초과하였다. 따라서 장항 지역에서 실제 구리의 농도가 이러한 빈도로 지속되는 경우 FMB에서 기준으로 하는 허용 빈도를 3년에 1번 보다 자주 초과하게 된다. 본 연구에서는 장항 공극수의 환경적 특성을 고려 하였을 때 FMB 기법을 적용하는 경우 해당 지역에서 실제 구리의 농도가 0.17 mg/L을 초과하지 않을 때 보리를 포함한 주변 식생을 효과적으로 보호 할 수 있다는 결과를 얻었다.

FMB의 개념을 공간적으로 확장하여 적용하기 위해 한강 수계 내 12개의 측정소를 선택하였으며 2014년 6월부터 2016년 10월까지 각 지역의 수질 특성을 고려한 구리의 예측 농도 값들을 BLM으로 산출하였다. 구리 이온의 농도와 칼슘 이온의 농도가 지역별로 동일하다고 가정하고 수계의 환경 인자들을 각각 반영 하였을 때 지역별 FMB 값은 2.63 μg/L에서 7.41 μg/L 사이에서 다양하게 분포하였다. 현재 국내 수계에서는 양이온의 농도와 구리 농도는 자동으로 측정하지 않고 있는데 산단하천 지역의 경우에만 한 달의 한 번 구리를 포함한 중금속 농도를 측정하고 있다. 칼슘 이온의 경우 생물체에게 독성을 띄는 것은 아니지만 구리 이온과 함께 수계에 존재하는 경우 생물체에 발현되는 구리 이온의 독성을 변화 시키는 요소로 작용할 수 있으며 칼슘 이온의 농도가 0 mM에서 2 mM로 변화하는 경우 해당 수계에서의 FMB 값 역시 3.999 μg/L에서 28.87 μg/L까지 달라지게 된다. 뿐만 아니라 구리 이온 분포의 표준편차가 각각 1, 1.1, 1.2, 1.3, 1.4, 1.5 일 때 FMB로 산정한 수계의 구리 허용농도는 4.30 μg/L에서 23.7 μg/L로 변화한다. 따라서 수계에서 생물에게 독성 영향을 발현하는 구리의 허용 농도를 보다 정확하게 예측하기 위해서는 칼슘 이온과 구리 이온의 농도를 주기적으로 측정 해야 한다.

주요어: Biotic ligand model, Fixed monitoring benchmarks, 구리 독성, 토양 공극수

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