論文要旨

Thesis Abstract

Contamination of Ciujung Watershed due to Mercury : Ecological risk assessment, Sources, and Mitigation

水銀による **Ciujung** 流域の汚染：生態学的リスク評価、発生源、および緩和について

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Monitoring of metal accumulation into aquatic biota or sediments and their toxicity is carried out to assess surface water quality and ensure food safety, as well as for compliance with the government regulations. Even though these activities are a very classical study, we believe that this study is still very actual and many aspects are still to be challenging to deal with. Therefore, in the last decade, the study of bioaccumulation or bioconcentration of organic and inorganic compounds in the fresh water and aquatic organism and their toxicities are still conducted by many researchers in the worldwide, particularly of heavy metal. It is used to identify the various metal contamination from natural or anthropogenic sources and assessment of ecological and also health risk, respectively.

Heavy metals, arsenic (As), chromium (Cr), cadmium (Cd), lead (Pb) and mercury (Hg), have a great attraction in aquatic environment. These pollutants have potential toxicity for human and aquatic organism due to persistent contaminants and bioaccumulate through the food chain. Several studies have demonstrated that oxidative stress and reactive oxygen species play a key role in the toxicity and carcinogenic of these metals in metabolism, detoxification and damage repair. In biological systems, long-term exposure of Cd can cause some disease for instance itai-itai disease, and kidney damage. Pb is associated with nervous system disorder and lead encephalopathy. As can cause arsenicosis, abnormality of Mee's line, diabetes melitus, and peripheral neuropathy; Cr can cause skin sensitization, transient renal effects; Pb can cause encephalopathy, henolytic anemia, hypertension, and cardiovascular disease; and Hg can cause mercurial tremor, immune dysfunction,

nervous system and gastrointestinal disturbance. Because of this fact, these five elements become a major concern of global pollutant.

Sediments are important as heavy metal pollution indicators in aquatic ecosystem since it is the primary sink for all metals in rivers. When the level of heavy metals concentration exceeds natural or permission limit, it can be adverse for human health via food chain.

Banten Province, one of the neighboring provinces to Jakarta city, has one the largest river namely Ciujung watershed. The Ciujung watershed plays an important source for sanitation and agriculture purposes. Since Banten is new province in a decade ago, the establishment of this province, as an effect of decentralization policy implementation, has created a new economic growth region in Java. Without a proper water quality management and planning, the economic growth in Banten Province is worrying to become worsened as what has happened in its neighboring city, Jakarta. The protest from resident to local government raise every year due to the degradation of the Ciujung water quality caused by heavy metal pollution. The improper of wastewater treatment from industrial activities which is directly discharged into the river and flows through the subsidence, dissolve the contaminants, and then subsequently deposit in sediments downstream is one of the root causes in the Ciujung watershed. Based on this, it highly appreciated to evaluate the contamination status of As, Cd, Cr, Hg and Pb in sediment of the Ciujung watershed using environmental water pollution assessment. In order to achieve the above goal, if we break down the main objective of the study into several Chapter.

Chapter 1 discuss about the general introduction and literature review. Chapter 2, 3 and 4 are the main chapter which focus on ecological risk assessment of heavy metals (As, Cd, Cr, Hg and Pb) in sediment of the Ciujung Watershed, identification of Hg sources, and method development for Hg removal in solid sample as a part of Hg prevention or mitigation, respectively. The last chapter is conclusion.

In the Chapter 2, sediment samples have been taken from eleventh sites from upstream to downstream included its tributaries. The sediment sample was collected in the rainy season after 1 d heavy rainfall. All heavy metals were measured by using spectrometric method using Flame AAS, HG-AAS and mercury analyzer. The mean heavy metal concentrations in the Ciujung Watershed and its tributaries were in the order Pb > Cr > Cd > As > Hg. Cd, Cr, and Pb had the highest concentrations (30.0, 22.0, and 23.0 mg kg^{-1}, respectively), while Hg had the lowest concentration (0.02 mg kg^{-1}). However, the levels of all heavy metals, except Hg, in the Ciujung Watershed were below the permissible limits set by ANZECC ISHG and Hongkong ISHG. In this study, the sediment Hg concentrations were higher than the foregoing sediment quality guidelines in nearly all streams except S1 (upstream). To measure the contamination levels of heavy metals in the Ciujung Watershed, "geo accumulation index (Igeo) , enrichment factor (EF) and potential ecological risk index (PERI) and biological effect (BE)" have been utilized.

According to the geo-accumulation index, As, Cr, and Pb belong to class 0 (uncontaminated), while Cd and Hg particularly in S5 had moderate Hg and severe Cd contamination, as its Igeo value was >5, which indicates extreme pollution.

According to the enrichment factor, The EF values for Hg in all streams, except S1 (0.3), exhibited moderate enrichment (5 < EF < 10). High EF values for Cd were observed for S1 (upstream) and the tributaries (T1, T2, and B1). They were in the range of 10–25, which indicated severe enrichment.

The potential ecological risk index of As, Cr, and Pb were less than 40 at all sites. It means the ecological risk was low in nearly all cases. High Cd PERI values were established for S1 (305), T1 (230), T2 (485), and B1 (410). These calculations suggested a high or extreme ecological risk, and the Hg PERI values were >160 in all sediments. Hence, all sites were at considerable to very high ecological risk. The average PERI values were in the order Hg > Cd > Pb > As > Cr. The foregoing results indicate serious Hg and Cd contamination in the Ciujung Watershed and its tributary.

Biological effect was evaluated based on ERMQ and PELQ values. The results showed that all heavy metals in all sediments indicated 30% warning level and 25% possible adverse toxicity to the inhabitants. In most sediments, Hg concentrations surpassed the PEL and ERM values. Hence, the Ciujung Watershed was polluted mainly by Hg and Cd. Therefore, Hg contamination in the

Ciujung Watershed should be investigated, in which this topic is focused deeply in Chapter 3.

Chapter 3 investigates the source of Hg contamination in the Ciujung Watershed. Author can infer that Hg released into the river, flown through, and settling, dissolving in the water, and getting deposited in sediments can lead to serious problems in downstream areas through the improper wastewater treatment from AGSM activities. ASGM activities could be the source of Hg in sediment of Ciujung watershed transported by tributaries. Due to Hg has strong correlation with dissolved organic matter (TOC, TN and POP) based on Pearson's correlation analysis, authors can investigate the source of Hg contamination in the Ciujung Watershed using molar ration of both organic C and N isotope ($\delta^{13}C$ and $\delta^{15}N$ values). An analysis of the C/N ratio together with $\delta^{13}C$ and $\delta^{15}N$ in the Ciujung watershed and its tributaries can provide information on the OM sources and identify the type of organic matter (OM). As predicted by the C/N ratio and $\delta^{13}C$ values, the mean $\delta^{13}C$ values indicated that the OM derived from the soil was abundant, where it was agrees with the soil organic properties of OM. A Bayesian mixing model was used to estimate the proportional contribution of each OM to the sediment at each site using the stable isotope and the three sources: S1 as uncontaminated upstream of the mainstream, T1 as a contaminated tributary (the Cisimeut River), and B1+B2 as a contaminated tributary (the Ciberang River). Based on the biplot of $\delta^{15}N$ and $\delta^{13}C$, OM, which accumulates sediment downstream of the Ciujung Watershed (mixtures S4, S5, and S6), had similar characteristics to the OM obtained from the mixtures T2 and B3; these sites were relatively close to the source (T1 and B1+B2). The contribution of soil OM from the Cisimeut River (T1) was found in most of the downstream sediment in S3–S6, in which the highest was S4 (60.8%), followed by S5 (49.3%), S3 (39.0%), and S6 (23.8%). The OM from the Ciberang River contributed to the downstream sediment in S3–S6, with the highest contribution in S6 (47.51%), S5 (36.3%), and S4 (26.0%) . It was revealed that the soil OM from the Ciujung and Ciberang Rivers, which contained Hg, contributed to the accumulation of Hg in the sediment in the downstream area of the Ciujung Watershed caused by a strong formation and complexation ionic bonds between mercury and soil organic matter affected the sequestration of mercury to sediment. The ecological risk of Hg toxicity based on risk quotient

(RQ) at the 11 sampling sites show that the RQs of 10 sediment sampling sites in the Ciujung Watershed included mainstream and tributaries are between 0.1 and 1, while the RQ of S1 is less than 0.1, indicating that overall, the ecological risk level of Hg in Ciujung sediment was moderate. Regarding this, we can infer that Hg contamination in the Ciujung watershed has potential effect to benthic organism as a food chain in most of sampling sites except S1 even the level of Hg risk is moderate. Future research is highly required to examine different species of fish and benthic organism from those sampling sites in the Ciujung Watershed.

Based on Chapter 2 and 3, the Hg contamination in the Ciujung Watershed showed potential ecological risk to the environment and aquatic organism. Thus, an attempt should be utilized to reduce/remove Hg content in the sediment or solid sample. This work is more deeply studied in the Chapter 4.

In the Chapter 4, authors developed a new technique for Hg removal in the Hg-contained sediment based on acid extraction. The method accurately removed Hg in the sediment and solid sample using hydrobromic acid (HBr) 15-48% v/v by combination of vortex agitation and ultrasonic irradiation. The method was validated by measuring CRM ERM CC580 with high of Hg concentration (Hg: 132 mg kg^{-1}) and CRM NMIJ 7302-a with low of Hg concentration (Hg= 0.52 mg kg^{-1}). The high efficiency of vortex and sonication time were obtained at 5 min and 6 min, respectively with extractability 101.14%. Overall, the Hg removal in sediment can be achieved within 21 min. This finding was faster than the other researcher by using combination of vortex and ultrasonic irradiation. Also, the method had been successfully applied in environmental matrices for instance sediment, soil and fish.

論文概要

堆積物は河川におけるすべての金属の主要な吸収源であるため、水域生態系の重金属汚染指標として重要である。重金属濃度のレベルが自然または許容範囲を超えると、食物連鎖を介して人間の健康に悪影響を与える可能性がある。

ジャカルタ市に隣接する州の 1 つであるバンテン州には、最大河川の 1 つである Ciujung 流域がある。Ciujung 流域は、衛生と農業の用途で重要な資源である。重金属汚染による Ciujung の水質の悪化により、住民からの地方自治体への抗議が毎年高まっている。河川に直接排出され、沈下、溶解によって汚染物質が流出し、その後下流の堆積物に堆積する産業活動からの排水の不適切な処理は、Ciujung 流域の根本的な原因の 1 つである。これに基づいて、環境水質汚染評価手法による Ciujung 流域の堆積物中の As、Cd、Cr、Hg、および Pb の汚染状態を評価することは高く評価されている。上記目標の達成のために、調査の主な目的をいくつかの章に分けて示した。

第 1 章では、序論と文献レビューについて示した。第 2 章、第 3 章、および第 4 章は、Ciujung 流域の堆積物中の重金属（As、Cd、Cr、Hg、および Pb）の生態学的リスク評価、Hg 源の特定、および固体サンプル中の Hg 除去の方法開発について、それぞれ水銀の予防または緩和の一部として示した。最後の章は結論とした。

第 2 章では、支流を含む上流から下流への 11 のサイトから堆積物サンプルが採取された。堆積物サンプルは、1 日間の大雨の後の雨季に収集された。すべての重金属は、Flame AAS、HG-AAS、および水銀分析装置を使用した分光分析法により測定された。堆積物の平均金属濃度は、Pb> Cr> As>Cd>Hg の順序であった。乾燥重量による平均 As、Cd、Cr、Hg、および Pb 濃度は、それぞれ 1.68±0.63 mg kg^{-1}、0.80±0.88 mg kg^{-1}、4.12±0.88 mg kg^{-1}、0.61±0.25 mg kg^{-1} および 19.80±7.51mg kg^{-1} であった。環境リスクは、地球蓄積指数（Igeo）、濃縮係数（EF）、潜在的な生態学的リスク指数（PERI）、および生物学的影響によって評価された。Ciujung 流域では、As、Cr、または Pb の深刻な汚染は見られなかったが、Hg および Cd の深刻な汚染が見られた。S1 サイトを除くすべてのサンプリングサイトにおいて、Hg（Cd ではなく）の濃度は SQGV および TEL/ERL に従って確立された許容限度よりも高かった。Hg の PERI 値は、S1 サイトを除くすべてのサンプリングサイトで 160 より大きかった。人力小規模金採掘（ASGM）に由来する水銀は、非常に高い生態学的リスクをもたらしていた。本研究は、Ciujung 流

域の堆積物表層における現在の重金属汚染状況を正確かつ包括的に描写した。調査結果は、規制当局が効果的な管理措置を策定および制定し、Ciujung 流域の住民の間で Hg 汚染についての意識を高めるのに役立つ可能性があることが示された。したがって、Ciujung 流域の Hg 汚染を調査する必要がある。このトピックに関しては、第 3 章で深く焦点を当てている。

第 3 章では、Ciujung 流域の Hg が AGSM 活動による不適切な排水処理が下流域で深刻な問題を引き起こしていたため、Ciujung 流域の Hg 汚染源を調査した。

ASGM はインドネシアで最大の水銀汚染の原因である。本研究では、炭素（δ13C）と窒素（δ15N）の安定同位体を測定することにより、Ciujung 流域の堆積物の汚染における ASGM によって生成された Hg の寄与を調べた。雨季の支流を含む 11 のサンプリングサイトから表層堆積物が収集された。その結果、ほぼすべてのサンプリングサイトの総 Hg 濃度 (THg) は 0.02〜0.91 mg kg^{-1} d.w.の範囲であり、底質の濃度限界を超えていた。水銀と全有機炭素、全窒素、粒子状有機リンの間には強い相関関係が見られた。δ15N は、堆積物中の水銀が同じ点源に由来することを明らかにした。C / N と δ13C の比率に基づいて、底質中の有機物は土壌有機物として特定された。有機物の δ13C と δ15N を用いたベイズ混合モデルは、Ciujung 流域の支流である Cisimeut 川と Ciberang 川がこれらの支流の上流域での違法な ASGM 活動による主流の Hg 汚染に寄与していることが示唆された。それらの相対的な寄与は 23.8%から 61.0%の範囲であった。生物学的効果は、ほとんどのサンプリングサイトの Hg 濃度が ERM および PEL 値を超え、S1（上流）を除くほぼサンプリングサイトの Hg のリスク指数（RQ）が 0.1 から 1 の間であったことから、Ciujung 流域の堆積物中の Hg 汚染が中程度であり、底生生物への潜在的な影響が大きいことが示された。

第 2 章と第 3 章に基づいて、Ciujung 流域の Hg 汚染は、環境と水生生物に対する潜在的な生態学的リスクがあることを示しました。したがって、堆積物または固体サンプル中の Hg の低減/除去について利用することを試みる必要がある。本内容については第 4 章で詳細に研究された。

第 4 章では、著者らは、酸抽出に基づいて、Hg を含む堆積物中の Hg を除去するための新しい手法を開発した。この方法では、撹拌と超音波照射の組み合わせにより、臭化水素酸 15〜48%を使用して、堆積物または固体サンプル中の Hg を効率良く除去できた。この方法は、高水銀濃度（Hg : 132 mg kg^{-1}）の CRM ERM CC580（河口堆積物）と低水銀濃度（Hg = 0.52 mg kg^{-1}）の CRM NMIJ 7302-a（海底

堆積物）を測定することによって検証された。ボルテックスと超音波処理時間の高効率は、それぞれ 5 分と 6 分で得られ、回収率は 101.14%であった。全体として、堆積物サンプル中の Hg の抽出性は 21 分以内に達成できた。この結果は、撹拌と超音波照射の組み合わせを使用することにより、他の研究よりも良好な結果であった。また、この方法は、土壌や魚などのさまざまな環境マトリックスにも適用できることが示唆された。

キーワード：Ciujung 流域、堆積物、重金属、水銀、生態学的リスク評価、安定同位体、臭化水素酸、撹拌、超音波照射。