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The Analysis of Heavy Metal Transport Mechanism and Electrolytic Reduction Method for Remediation of Agricultural Ditches

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Abstract: The complex sources of heavy meatal pollution in agricultural lands include: inappropriate discharge, contaminated irrigation water, fertilizer application and atmospheric fallout. The excessive heavy metal concentration can affect crop production and quality. In Taiwan, there are more than 1000 hectare of contaminated agricultural lands, which are mainly located in Taoyuan, Changhua and Kaohsiung. This study aims to analyze the heavy metal concentration in water and the bottom mud to establish the water-sediment heavy metal transport model for the agricultural ditches, Sankuaizho, in Taoyuan, and further evaluate the effect of heavy metal desorption by the electrolytic reduction method. The research results showed that the water body of the Sankuaizho is mainly polluted by heavy metals such as Cu, Ni, and Zn, but only Cu exceeds the water quality standard for irrigation (> 0.2 mg/L). The sediment is polluted by heavy metals, such as Cr, Cu, Ni, Pb and Zn, especially Cu pollution is the most severe one. The electrolytic reduction method could effectively remove heavy metals from bottom mud in terms of the electrolytic reduction efficiency ranged between 43.93% and 97.52%. The WASP simulation results showed that the concentration of heavy metals (copper, zinc, and nickel) at the most downstream (segment 7) are highest when mixed with the polluted water from the upstream flow, which is mainly resulted from the effluent from the electronics factory. Compared to the observed data, the MAPE values of model simulation results are: copper = 47.12%, zinc = 26.62%, nickel = 36.66%, showing that the WASP model performs well and reasonably. The research results of this study could be used as a reference for future decision making to improve the water quality and solve the bottom mud issues.

Key words: heavy meatal pollution, agricultural ditches, WASP8, electrolytic reduction method

1. Introduction

Due to the rapid development of industrialization and urbanization, artificial wastewater (agriculture, animal husbandry, factory and household wastewater, etc.) is discharged into rivers and groundwater. When untreated wastewater is discharged into rivers with high concentration of heavy metals, the concentration of heavy metals in rivers increases rapidly. They are deposited on the river bed during dry seasons, and the accumulated chemicals will directly or indirectly affect organisms and water ecology [1-4].

After the heavy metals are discharged into rivers, they will settle to the bottom of the water by gravity during the flow of the river, and the dissolved metal ions will be stored in the sediment by precipitation, ion exchange, adsorption or complexes. Even the concentration of heavy metals in the water is not high, the concentration of the sediment could be much higher than that of the water and the air due to long-term adsorption and accumulated in the sediment [5]. Sediments may change depending on water quality or environmental conditions, such as pH, redox potential, or the presence of organic complexing agents, heavy metals in the sediment may be released into the water again, absorbed and accumulated by

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organisms in the water, and have a negative impact on the sediment. Human health and ecological environment pose potential hazards [6]. In an oxygen-poor environment, when sediment is disrupted and becomes an aerobic environment, its acid neutralization capability (ANC) decreases, resulting in a decrease in pH value, which increases the mobility of metals in an acidic environment. Subsequently released again into the water [7]. In recent years, sediments have been regarded as one of the main sources of non-point source pollution in the environment and the concentration of heavy metals in the water [8]. Owens P. et al. pointed out that rivers and lakes will face two major environmental problems in the future, such as a large increase in the amount of sediment pollution and high toxic substances, especially in the lower reaches of large rivers and coastal areas.

Sediments play an important role in both source and sink terms in the transport of pollutants. Heavy metals move in the sediments, so that the sediments can not only store heavy metals in the water, but also transmit heavy metal pollutants at the same time. The transport of heavy metals from sediments to river water is regarded as a reversible process. Heavy metals can be caused by geochemical reactions and resuspension of sediments due to changes in the river flow field or disturbance of the bottom of the river bed. Resuspension of the water body results in an increase in the concentration of heavy metals in the water.

Cost is an important factor in assessing techniques for handling and disposing of sediments. The properties of sediments are between soil and sludge, and the contaminated sediments generally only needs to be pre-treated (or without pre-treatment), so it can be decontaminated using related technologies. For heavy metal pollution in soil and sediments, the traditional remediation and restoration method is to remove the pollutants by engineering techniques such as physicochemical treatment. The main drawbacks of this type of technology are the adverse effect of treatment and the high cost of treatment. Traditional treatment technology also includes curing treatment. It has the advantages of short reaction time, better efficiency, and less space requirement, however, its drawbacks such as the high cost of treatment and lack of respect for the environment are the greatest limitations in the application [10]. Moreover, the cured product after curing treatment still needs to be buried and disposed, and the long-term stability is not good, which may cause the leakage of heavy metals and cause secondary pollution problems. Today's environmental technology has shifted the focus from the traditional end-of-pipe treatment to pollution prevention and resource recycling. The cost is more reasonable, with little environmental impact. Among them, electrolytic reduction is a method commonly used domestically and internationally. It has the advantages of simple operation, a good treatment effect and absence of chemical pollutants, making this method the most potential physicochemical treatment procedure today.

Sediments act as a storage tank because of the long-term accumulation of pollutants, sludge, garbage and other pollutants in the sewage of factories, livestock and households. The body of water in the river, these polluting particles settle and accumulation as a result of the action of gravity or the slowing down of the river flow rate, causing in high concentrations of chemicals and heavy metals in the sediment [11]. This study proposes that when the river rate is slower than 0.18-0.30 m/s, pollutants are easy to precipitate and accumulate at the bottom of the river to form sediments. However, when the flow velocity is greater than 0.30-0.45 m/s, erosion will occur, and the sediment at the bottom of the river may be turned over again, leading to an increase in suspended solid and organic matter in the water body.

WASP, a water quality model, is capable of simulating changes in the water quality after human activities, including general normal pollutants: ammonia nitrogen, phosphorus, dissolved oxygen, biochemical oxygen demand and nutrients, etc. The simulation of the transmission of water bodies such as rivers, lakes and reservoirs, related research: Ernst M. R., Owens J. J. L. and Management R. used WASP to assess the pollution sources from the eutrophication Cedar Creek Reservoir, and found that the chlorophyll and total phosphorus concentration in the reservoir were most impacted by non-point source pollution in the watershed; Yang C. P., Yu Y. T. and Kao C. M. simulated changes of BOD and ammonia nitrogen flux in Gaoping River under climate change.

2. Material and Methods

2.1 Study Area

According to the report of National Taiwan University (2016), the survey data of channel sediments in Luzhu and Dayuan District from 101 to 102-year showed that the heavy metal project with the lowest pass rate was copper (22.5%), followed by zinc (53.5%) and nickel (71.8%). Therefore, this project will use the monitoring data of copper and heavy metals in the Sankuaicuo Tributary (Fig. 1) as a reference for the investigation of heavy metals in the channel sediments and the establishment of the water-heavy metal pollution transmission model. The Sankuicuo Tributary belongs to the Pusin River Basin, the third Tributary of Taoyuan Aqueduct. Taoyuan Aqueduct spans Xinwu District, Guanyin District, the north of Zhongli District, and the east of Neili District. The terrain slopes from southeast to northwest. The annual average temperature in Taoyuan City is about 21°C, the average temperature in summer is about 27°C, and the average temperature in winter is about 15°C. The average annual rainfall is about 2,000 mm, but the rivers in the area are short, the rainwater retention time is short, and the water source that can be used is limited. The water source of Taoyuan Aqueduct's irrigation area is mainly from Shihmen Reservoir (accounting for 47%), while the sources of river water include Nankan River, Jiadong River, Sinjie River, Laojie River, Shezi River, Sinjhuangzih

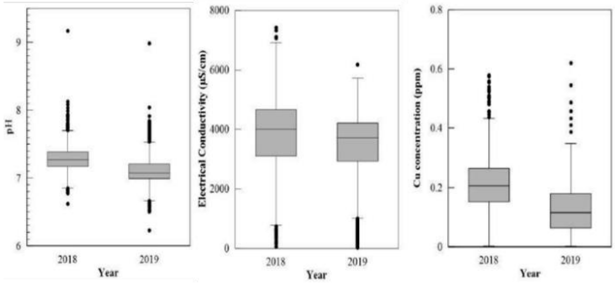


Fig. 1 Annual average pH, EC and Cu concentration in Sankuicuo.

River, etc. The amount of water diversion accounts for about 53% of the irrigation water source. The irrigation system in the irrigation area is mainly composed of Taoyuan Aqueduct, pond and river weirs. The total length of the trunk line is 15.42 km, and the Tributary is 322.92 km. The total length of roads is 2,658.84 km, and the drainage road is 1.16 km (National Taiwan University, 2016).

2.2 Field Study

Referring to the 2016 survey report of National Taiwan University and the monitoring points of the Agricultural Engineering Research Center, eight sampling points were set up on the Sankuicuo Tributary, of which there were three sampling points (Sankuaicuo 1, Sankuaicuo 6, Sankuaicuo 7). At the same time, the sediments were taken to the laboratory for electrolysis analysis of the sediments. The configuration standards included the upper and lower boundaries of the model, the water body was not affected by the effluent from the electronics factories, the water body was affected by the mixing of the effluent from the electronics factories, and the mixed water body, whether they met the irrigation water quality standards.

This project planned to conduct manual sampling on the site once a month. The water sampling method was in accordance with Environmental Protection Agency (EPA) "General Provisions of Water Sampling for Rivers, Lakes and Reservoirs (NIEA W104.51C)". The sediment sampling method followed EPA sediment sampling method (NIEA S104.32B), the collected sediment samples were put into No. 11 ziploc bags, brought back to the laboratory.

2.3 Water and Sediment Analysis

The water analysis was complied with the general rules of heavy metal detection methods of EPA (NIEA M103.02C), and the inspection equipment was inductively coupled plasma-atomic emission spectrometry (ICP-AES). The quantitative limit is 0.005 mg/L. The collected water samples were added with an appropriate concentration of nitric acid, and then filtered by Teflon (PTFE) with a pore size of 0.22 μm. The concentration of eight heavy metals in the water could be tested by an ICP-AES.

The sediment analysis was complied with "Determination of Metals in Soil-Microwave Assisted Aqua Regia Digestion" of EPA (NIEA S301.61B), and the inspection equipment was ICP-AES. Since the collected sediments contained moisture, sediments must be dried first and then 0.5-1.0 g of sediments should be homogenized and placed in a digestion bottle. After capping, put it into a microwave digestion system, and reacted at a high temperature of 175°C. After 10 minutes, poured the solution in the digestion bottle into a volumetric flask after cooling, and then ICP-AES could be analyzed. Finally the concentration of heavy metals in sediments is calculated.

2.4 Water Quality Model

WASP model was first developed by the Manhattan College Laboratory, and then jointly developed and modified by USEPA. WASP model simulation projects include: basic water quality parameters (pH, water temperature, etc.), suspended solids, nutrients, algae and toxic substances (heavy metals, mercury, plastics, petroleum, chlorine compounds, pesticides, nanomaterials, etc.). Heavy metals include: copper, lead, zinc, cadmium, arsenic, tin, selenium, chromium. WASP7 is divided into eight modules according to the nature of the pollutants, namely, Eutrophication, Advanced Eutrophication, Simple Toxicant, Non-Ionizing Toxicant, Organic Toxicants, Mercury, and Heat. Four types of toxic metal modules (Meta4), which can establish one-dimensional, two-dimensional and three-dimensional dynamic water quality simulations. It can simulate and analyze multiple types of water bodies, such as ponds, streams, lakes, reservoirs, and tidal/non-tidal rivers, estuaries, coasts, etc. The main principle of its simulation is mass balance, which can effectively simulate the diffusion, input, and transmission of point source pollution. Considering the sorption, sedimentation, and resuspension process of nutrients and toxic substances on suspended solids, and then simulate the interaction between river water quality and river sediments.

In addition to simulating one-dimensional, two-dimensional, and three-dimensional water problems, and analyzing various water quality problems and various types of water, WASP model can also analyze multiple kinds of pollutants, including conventional pollutants (such as dissolved oxygen, nutrients, etc.) and toxic chemicals. Time-variant or time-invariant, linear and nonlinear analysis, and point and non-point source pollution can also be considered. WASP can be combined with hydrodynamic and watershed models, allowing multi-year analysis under different meteorological and environmental conditions. The hydraulic model is used to simulate the results of hydraulic phenomena, and then imported into WASP to make the water quality simulation more comprehensive; pollutants can also be imported into the pollution loading model [14].

WASP uses a finite grid as the numerical method. Pollution transmission simulation is calculated by parameters such as deoxygenation, nitrification, re-aeration and natural degradation reactions, and they meet the mass balance condition.

The main control equations of the mode are as follows:

Water quality control equation:

$$\frac{\partial C}{\partial t}+\frac{\partial UC}{\partial x}-\frac{\partial\left(E_x\frac{\partial C}{\partial x}\right)}{\partial x}-\frac{\partial\left(E_z\frac{\partial C}{\partial z}\right)}{\partial z}=S_L+S_K \qquad (1)$$

Sediments control equation:

$$\frac{\partial C}{\partial t}-\frac{\partial\left(E_z\frac{\partial C}{\partial z}\right)}{\partial z}=S_K \qquad (2)$$

Among them, U is the x-direction flow velocity (m/s), C is the pollutant concentration (g/m^3), E_x, E_z are the x- and z-direction dispersion coefficients (m^2/s), S_L is the external load (g/m^3/s), S_K is the source-sink term (g/m^3/s).

In water, the conversion equation between the dissolved state and the adsorption state of heavy metals:

$$C_t=C_{td}+C_{tp} \qquad (3)$$

$$C_{td}=\frac{C_t}{1+K_dSS}=F_dC_t \qquad (4)$$

$$C_{tp}=\frac{K_dSSC_t}{1+K_dSS}=F_PC_t \qquad (5)$$

C_t is the total concentration of heavy metals (g/m^3); C_{td} is the dissolved concentration (g/m^3); C_{tp} is the adsorbed concentration (g/m^3); SS is the total amount of suspended matter (g/m^3), and K_d is the adsorption coefficient (L/g).

2.5 Remediation Method

The sediment samples collected in this project were preliminarily divided into two parts, one part was analyzed by ICP-AES for the original heavy metal content of soil samples, and the other part of the same batch of soil samples was for electrolytic reduction experiments. The soil samples were grouped into experimental group and control group. The control group uses a high current density to quickly analyze the adsorption efficiency in a short time; the experimental group uses a low current density and a long reduction time to fully reduce the adsorption efficiency in the sediments. Heavy metal ions, combined with electrode materials and shapes design to improve adsorption efficiency, calculate the cost-effectiveness ratio by applying the current density, time and electrode material, and expect to find the most reasonable cost.

The experimental group method of this experiment would simulate the concentration of copper ions in the sediment by adding copper sulfate. During the experiment, a solution of known copper sulfate concentration would be added to the sediments, and the sediments will be measured after the electrolytic reduction process. At the same time, the weight of copper on the surface of the reduction electrode was measured, and the efficiency of electrolytic reduction of copper in the sediment was further converted. In the control of this experiment, the actually collected sediments were used as the object of electrolytic reduction of copper, and the copper ions concentration in the sediments before and after electrolytic reduction was measured to evaluate the efficiency of electrolytic copper reduction.

In the reduction reaction of metal ions in the electrolyte (Fig. 2), the electrolyte can be regarded as the sediments containing heavy metal ions, the cathode can be regarded as the working electrode or the heavy metal ion adsorption electrode, and the anode can be regarded as the opposite electrode or an ion-conducting electrode. When a direct current is passed between the two electrodes, the heavy metal ions in the sediment will dissociate to the surface of the cathode and be reduced to a solid heavy metal film in atomic form. Common heavy metals are in the sediment, including copper, nickel, zinc, lead, and so

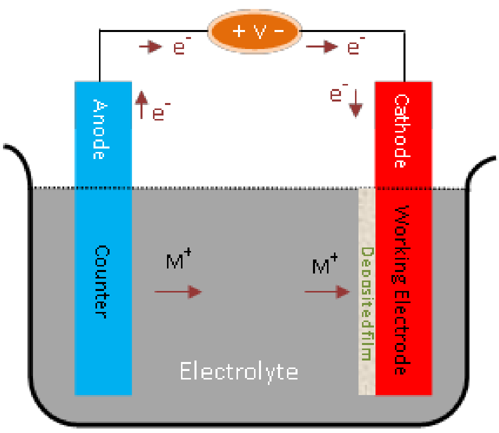


Fig. 2 The reduction reaction of metal ions in the electrolyte.

on. The Pourbaix diagram shows that, in alkaline electrolytes, Cu^{2+} is reduced to Cu, Ni^{2+} is reduced to Ni, Zn^{2+} is reduced to Zn, and Pb^{2+} is reduced to Pb, the reduction voltages are 0.34, -0.25, -0.76, -0.13 VSHE, respectively.

The reduction efficiency of heavy metals in the sediment is primarily influenced by soil conductivity and the concentration of heavy metals. The principal reaction formula in the process of reducing heavy metal is $Metal2^{+} + 2e^{-} \rightarrow Metal$. According to Faraday's laws, the relation between the applied current value and the weight of the reduced heavy metals is calculated. The relation can be expressed as Eq. 5 and simplified to Eq. 6:

$$Q = IT = nFN = n\frac{FW}{M} \tag{5}$$

$$W = \frac{ITM}{nF} \tag{6}$$

Q: Electricity (C), I: Current (A), T: Time (sec), n: dissociation valence, F: Faraday constant (96500), N: Mole number (mole), M: Molecular weight (g/ mol).

The heavy metal reduction efficiency (η) can be further calculated as follows:

$$\eta = \frac{100\% W_a}{W} \tag{7}$$

W_a is the weight of the heavy metals actually reduced, and W is the weight of the heavy metals theoretically reduced.

3. Results and Discussion

3.1 Remediation Results

The main operating parameters is the electrolytic reduction method, including the voltage, the current, the temperature, the cathode working electrode, the anode working electrode, the electrolyte, stirring of sediments, and electrolysis time. The parameters and operational conditions of the electrolytic reduction method in this experiment are as follows: the voltage: 20 V; the current: 0.1 A; the temperature: 25°C, the cathode rod: stainless steel plate; the anode rod: graphite; the electrolyte: 5 vol.% sulfuric acid solution; the magnet stirring speed: 200 RPM, and the electrolytic reduction reaction time: 0.1 ~ 3 days.

The results showed that the sediments contained chromium, copper, nickel, lead, and zinc, and the copper ions pollution was the most serious. Exceeding the lower limit of copper concentration (50 mg/kg) of the sediment heavy metal control standard, the concentration of other heavy metals was within the lower limit of control. In the future, relevant agencies still need to conduct more detailed investigations on the target area when they implement comprehensive remediation. However, there were a few experimental data that the concentration of heavy metals after electrolysis was higher than that before electrolysis. It could be due to uneven distribution of heavy metals in the sediments, leading to using different layers of sediments for the same batch of sediments samples for electrolytic reduction analysis. Therefore, we extended the electrolytic reduction time to two days. In the two days, the ceramic stirrer continued to stir to make the sediments uniform into a fine texture and then be electrolytic reduction, and recorded the experimental results for two days. The electrolytic reduction efficiency [(heavy metal concentration before electrolysis — Heavy metal concentration after electrolysis)/heavy metal concentration before electrolysis * 100%] minimum 43.93%, maximum 97.52%.

3.2 Water Quality Model Simulation

Before the verification of the water quality model, the rate and value of various water quality parameters are often estimated based on previous literature or measured data, and then the water quality parameters in line with the characteristics of the river are obtained by adjusting the simulation. Considering the variability of sediment parameters, WASP model will additionally set up a sediment grid (the number is consistent with the water grid) to evaluate the interaction and influence of the channel heavy metal copper in the water body and sediment over time.

Table 1 The electrolytic reduction efficiency.

Date	Sampling no.	Electrolytic reduction efficiency (%)							
		As	Cd	Cr	Cu	Hg	Ni	Pb	Zn
9/17	S1	-	-	82.40	-3.92	-	78.10	24.71	70.42
	S6	-	66.67	46.26	21.54	-	47.32	41.87	79.26
	S7	-	-	81.84	6.23	-	74.21	16.16	31.14
11/3	S1	-	-	-	-	-	-	-	-
	S6	-	-	51.64	96.47	-	70.49	76.79	97.52
	S7	-	-	87.50	72.47	-	90.55	81.82	93.55
12/3	S1	-	-	-	-	-	-	-	-
	S6	-	-	53.93	46.30	-	43.93	45.95	75.20
	S7	-	-	-	-	-	-	-	-

In this study, the Advanced Toxicant module in WASP model is used for the simulation work. According to the designed sampling points, Sankuaicuo Tributary are divided into 7 river sections (grids); the sediments are also 7 grids, the total of 14 grids, each grid is set separately for the volume, the flow rate, the depth, the grid type and other parameters, the sediment volume and the sediment flow rate are assumed to be 0.1 times that of the water body (National Taiwan University, 2016). The simulation time is 1 month. The flow rate of Sankuaicuo Tributary is 0.44cms.

The simulated changes of the three heavy metal concentrations all indicate that the most downstream of the model (reach 7) will have the highest concentration of heavy metals when mixed with the polluted water flowing down the upstream. To improve the reliability of the model, WASP model calibration and verification operation is carried out using the sampling points set up in Sankuaicuo Tributary of this project. The results of the calibration and verification use the measured values at the sampling points. The verification value adopts the mean absolute percentage error method (MAPE). The calculation method is as follows. The smaller the value is, the closer the simulated value is to the measured value.

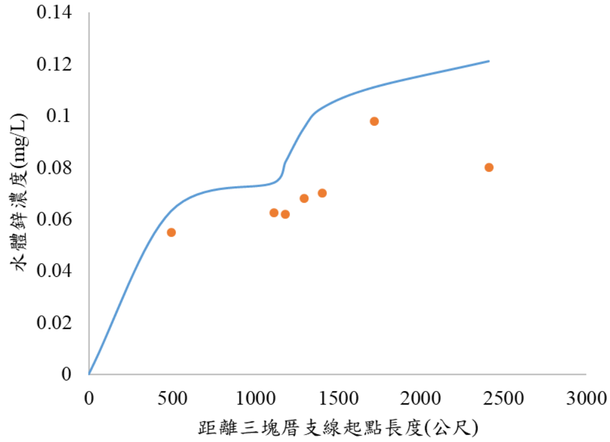
$$MAPE = \frac{1}{n}\sum_{t=1}^{n}\left|\frac{A_t - F_t}{A_t}\right| \qquad (8)$$

where n is the number of fitted points, A_t is the actual value, F_t is the forecast value.

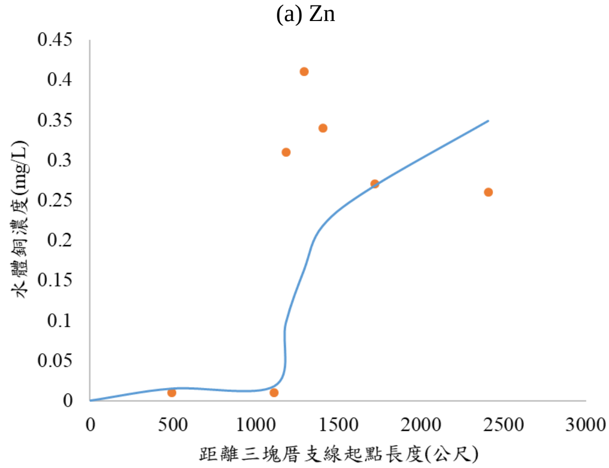
The simulation results of heavy metal concentrations are compared in water and the calibration verification results (Fig. 3). The figures clearly showed that the concentration of the three heavy metals gradually increased at about 1200 meters, which was the discharge port of the electronics factories. The discharge water from the electronics Factories was one of the main sources of water heavy metal pollution of Sankuaicuo Tributary. This result was also consistent with the research results conducted by AECOM Engineering Consulting Co., Ltd. in 2016. MAPE values of the measured data at sampling points and model simulation results in this study are copper = 47.12%; zinc = 26.62%; nickel = 36.66%, indicating a reasonable predictive capacity for the model.

4. Conclusion

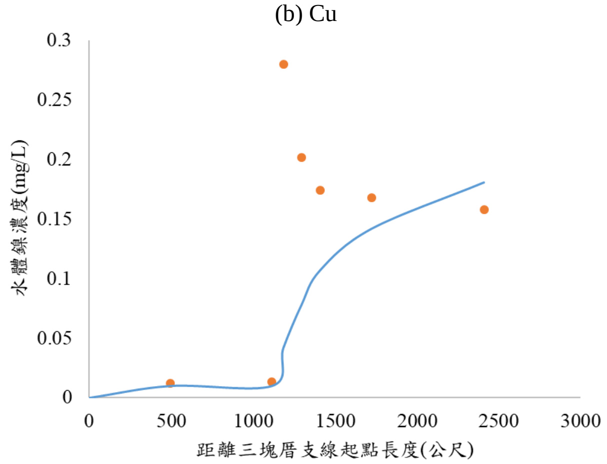
The study aims to set up the water-sediment transmission model of the heavy metal pollution channel and to analyze the effectiveness of the laboratory electrolytic reduction method to remove heavy metals in the sediments. The results of the heavy metals concentration analysis in the water quality of Sankuaicuo Tributary showed that the water body contained copper, nickel and zinc, and the heavy metal input route was the discharge water of the electronics factories. The sedimentation of the channel



(a) Zn



(b) Cu



(c) Ni

Fig. 3 Comparison of simulated and observed metal concentrations of water.

sediments is a natural phenomenon, but in actual situation, the sediments would be washed away by heavy rain and taken away from the original location, resulting in no sediments to be collected during sampling. Therefore, it is recommended to be careful of the onsite climatic conditions before collecting sediment samples.

On-site records and analysis data show that occasionally exceeding the standard occurs, but it is inaccurate to judge whether the water quality meets the standard for irrigation water only based on the average data. It is recommended that water quality samples should be tested and analysed in a long-term and fixed frequency.

During the initial electrolytic reduction experiment, there were several experimental data that the concentration of heavy metals after electrolysis was higher than that before electrolysis, and it was judged that the distribution of heavy metals in the sediment was uneven. Therefore, the original experimental method was adjusted and the electrolytic reduction time was extended to two days, and the ceramic stirrer continued to stir to make the sediments uniform into a fine texture and then be electrolytic reduction. The experimental results of this method are satisfactory. After mixing evenly, and adjusting the electrolysis time, the electrolytic reduction efficiency could reach more than 43.93%. Therefore, in the laboratory-scale experimental stage, it is recommended to lengthen the electrolytic reduction time and homogenize the sediments, which can effectively remove the heavy metals from sediments.

The results can be used as a reference for future practical feasibility, and can be applied to other key farmland channels with high pollution potential or channel sediments that have been polluted by heavy metals to need to be rectified, hoping to solve the problem of heavy metal pollution on-site channel sediments.

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