

# The Influence of Land Use and Fish Farming on the Contents of $\text{Ca}^{2+}$ , $\text{Mg}^{2+}$ , $\text{K}^+$ and $\text{Na}^+$ in Pond and Reservoir Ecosystems in an Agricultural Small Watershed, China

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## Abstract

It is not understood well that how the effects of land use and fish farming on the contents of alkali metals ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^+$  and  $\text{Na}^+$ ) in small water bodies of pond and reservoir ecosystems at the watershed scale. In this study, the concentrations of  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^+$  and  $\text{Na}^+$  in water bodies were measured for 103 ponds and reservoirs used as fish farming or surrounded by different agricultural land use types in the subtropical hilly watershed of Jinjing (105 km<sup>2</sup>), China. The two important environmental factors of fishing farming and agricultural land use influenced the spatial variation the contents of alkali metals. The ponds and reservoirs in residential area had significantly higher concentrations of  $\text{Ca}^{2+}$  and  $\text{Na}^+$  than those with other land use types, reflecting the influence of domestic wastewater. Compared with those of natural ponds with non-fish farming, no significant increase of alkali metal contents occurred in fish farming ponds, due to the regular cleaning of ponds by farmers. However, the effect of fish culture on alkali metal contents was still supported indirectly by the fact that the alkali metal contents significantly correlated with nitrate contents in fish farming ponds and but high related with that of DIP in natural ponds. The suitability assessment for irrigation on the pond water indicated that almost all of ponds were suitable for irrigation except some ponds surrounded by residential area and tea plantation. Generally, our results demonstrated that fish farming and agricultural land use affected the contents of alkali metals in ponds and reservoirs. The agricultural water irrigation would be with caution from the ponds with tea plantation and residential area in the subtropical hilly watershed.

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## Keywords

Land Use, Alkali Metals, Fish Farming, Agricultural Small Watershed, Pond and Reservoir

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## 1. Introduction

Ponds and reservoirs are generally small surface depressions that hold still and shallow water [1] [2]. The global number of small ponds ( $<0.001 \text{ km}^2$ ) is estimated to be  $5.47 \times 10^8 - 3.2 \times 10^9$ , with great uncertainty owing to failure to be detected by traditional satellite [3]. Thus, the importance of ponds has been ignored in the ecosystems. In recent years, the ecological function of ponds for ecosystems and climate change has gained more and more attention [4] [5]. Farming ponds serve as ecological functions of hydrological regulation, pollution mitigation, biodiversity conservation and socioeconomic benefits in China [1].

Water quality of ponds and reservoirs is of great importance for aquaculture production and the growth and yield of crops [6] [7] [8]. In China, ponds and reservoirs provide irrigation water for 39% of the total agricultural land [1]. Thus, it is important to assess the irrigation suitability of pond water so as to make appropriate management decisions [6]. Previous studies demonstrated that land use change and fish farming are important factors of affecting surface water quality [9] [10] [11] [12] [13]. Farming land was generally linked to excessive nutrients of surface water [14]. Residential land use exerts a major effect on nutrients as well as alkali (earth) metals owing to animal and human excreta and the use of table salts, disinfectants, and food additives in daily life. Intensified fish breeding ponds posed serious threat to the surface water quality since a large portion of biogenic elements in the fodder was not utilized by fish. In addition, agrichemicals like quick lime, calcium hypochlorite and potassium permanganate were used as disinfectants to prevent fish disease, which led to high levels of major metal cations [9].

Many studies focus on the cycling of nutrients in ponds [15] [16] [17], whereas much less attention is paid to alkali metal and alkaline earth metal cations such as  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$  and  $\text{K}^+$ . These metal cations are necessary to maintain the normal function of living organisms. For example, the ions of  $\text{Mg}^{2+}$  is involved in some enzyme-catalyzed reactions in the human body and also essential to chlorophyll synthesis in plants [18]. However, excessive contents of these cations in water bodies would have adverse impact on human health and ecosystem. For example, high levels of  $\text{Na}^+$  in soil tend to displace  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ , which would reduce the soil permeability and consequently affect the growth and yield of crops [19] [20] [21].

Ponds and reservoirs are widely distributed across southern China due to its abundant precipitation and agricultural demand, such as fish farming and paddy planting [1]. To explore the impacts of land use and fish farming on the geo-

chemical behaviors of alkali (earth) metals, we determined the concentrations of alkali metals ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$  and  $\text{K}^+$ ) of water bodies from 103 ponds under the influence of different land use and/or used for fish farming in southern China. The suitability of pond water for irrigation was finally assessed to the help farmers and policy-makers make related management strategies to better play valuable role of ponds.

## 2. Materials and Methods

### 2.1. Study Area

The headwater watershed of Jinjing (105 km<sup>2</sup>) was selected as the study area in a hilly subtropical region of the Hunan Province, China. The annual precipitation in the study area ranges from 1200 to 1500 mm, and the elevation ranges from 56 m to 434.8 m. The land use in the study area is dominated by three major types, namely forest, paddy fields, and tea plantations, which account for 58.5%, 31.6%, and 4.3% of the total area, respectively. 5.6% of the remaining areas are waters and residential ones. In areas like this, agricultural products and aquaculture are generally the main sources of income for farmers. In the study area, there are approximately 2010 ponds with a density of 20 ponds per km<sup>2</sup>, and more than 60% of these are used for aquaculture [22]. In our study, 103 ponds and reservoirs were randomly selected to observe the alkali metal contents of the pond water bodies

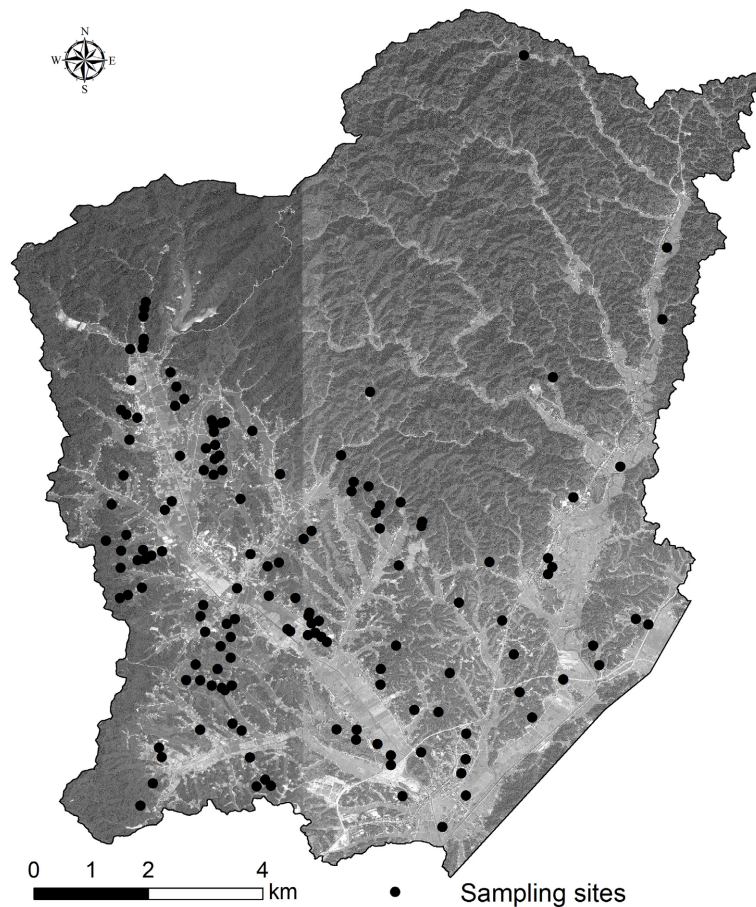
### 2.2. Water Sample Collection and Analysis

The water samples were collected below the surface of 30 - 50 cm in July 2019 from 103 ponds and reservoirs with different land use (32 for forest, 10 for tea plantation, 22 for farmland, 25 for residential area and 14 for mixed area (Figure 1). The 60 ponds are used for fish farming. The remaining 43 ponds are natural ponds without fish farming. All water samples were filtered through 0.45 μm membrane filters to Remove non-dissolved solid particulate matter within 24h after sampling and stored at -20°C until analysis. The concentrations of alkali (earth) metals ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$  and  $\text{K}^+$ ) were measured by inductively-coupled optical emission spectrometry (ICP-OES, 720-ES, USA) with an error of ≤5%. Water samples were transported to the laboratory where various N and P fractions, such as total nitrogen (TN), ammonium ( $\text{NH}_4\text{-N}$ ), nitrate ( $\text{NO}_3\text{-N}$ ), particulate nitrogen (PN), total phosphorus (TP), and particulate phosphorus (PP), were determined. The alkaline potassium persulfate digestion-UV spectrophotometric method was used to measure the contents of N fractions, and sulfuric/perchloric acid digestion-spectrophotometric method for ones of P fractions.

## 3. Results and Discussion

### 3.1. Statistical Description of Alkali Metal Contents

In order to examine the influence of human activities, the data of alkali metals



**Figure 1.** The spatial distribution of pond samples in the subtropical hilly watershed of Jinjing, China.

concentrations was classified into two groups. One group was used as natural ponds versus fish farming ponds. The other one was for natural ponds surrounded by the different land use types (tea plantation, residential area, forest and agricultural land). High variability of the concentrations of  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$  and  $\text{K}^+$  occurred in water bodies of ponds, with the corresponding average values of  $12.00 \pm 5.68 \text{ mg}\cdot\text{L}^{-1}$ ,  $10.61 \pm 6.55 \text{ mg}\cdot\text{L}^{-1}$ ,  $2.47 \pm 1.05 \text{ mg}\cdot\text{L}^{-1}$  and  $5.44 \pm 2.87 \text{ mg}\cdot\text{L}^{-1}$ , respectively. Fish farming ponds increased the contents of each of the four alkali metals than the natural ponds, but the increase was not all significant ( $P > 0.05$ ). The effect of land use types on each of the alkali metal contents varied considerably. There were not significant differences of  $\text{K}^+$  and  $\text{Mg}^{2+}$  levels among the land use types of tea plantation, residential area, forest and agricultural land. In contrast, the ponds had higher concentrations of  $\text{Ca}^{2+}$  and  $\text{Na}^+$  in residential land than those with other land use types.

In summary, the ponds in residential area had significantly higher  $\text{Ca}^{2+}$  and  $\text{Na}^+$  concentrations. Many studies revealed that increase in  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  and  $\text{Na}^+$  reflected the influence of domestic and industrial wastes [23] [24] [25]. Domestic wastewater is characterized by high  $\text{Na}^+$  contents, which resulted mainly from the animal and human excreta as well as the use of table salts, disinfectants, and

food additives. Thus, the higher  $\text{Ca}^{2+}$  and  $\text{Na}^+$  concentrations of ponds in residential area indicated the impact of domestic wastewater [24]. Fish farming ponds were expected to show significantly higher contents of  $\text{Ca}^{2+}$  and  $\text{Na}^+$ , because the disinfectants of quick lime, calcium hypochlorite, potassium permanganate and salt, were used to prevent fish disease [9]. However, the  $\text{Ca}^{2+}$  and  $\text{Na}^+$  contents were not consistent with the above hypothesis in the study watershed. One reason might be related to regular clearing of ponds by fishermen. In our study area, the management practices that fishman often change pond water, effectively reduced the accumulation of  $\text{Ca}^{2+}$  and  $\text{Na}^+$ .

### 3.2. Impacts of Anthropogenic Activities on Geochemical Behavior of Alkali Elements

Although the pool of alkali metals did not show significant variations, the geochemical behaviors could be altered due to the changes in redox conditions and fishing disturbance. Thus, the correlation matrix analyses were used to explore the response of geochemical behaviors of alkali elements to the different human activities.

#### 3.2.1. Impacts of Fish Farming

Quick lime and salt are commonly used as disinfectants in fishponds to prevent fish disease. Moreover, the feeding stuff is thought to be a major contributor to increase in nitrogen and phosphorus of fishponds [9]. These kinds of fishing practice might affect the geochemical behavior of alkali metals. To study the influence of fishing practices on alkali elements, the correlation of alkali elements and different N and P components was presented in the context of forest land use with fish farming ponds vs. natural ponds (Table 1).

**Table 1.** Pearson's correlation coefficient between alkali elements and nutrient elements in the context of forest land use.

	$\text{Ca}^{2+}$	$\text{K}^+$	$\text{Mg}^{2+}$	$\text{Na}^+$	DOC	$\text{NO}_3^-$	$\text{NH}_4^+$	TN	TP	PP	DIP
$\text{Ca}^{2+}$	1	-0.159	<b>0.693**</b>	<b>0.704**</b>	0.150	<b>0.516*</b>	0.281	<b>0.433*</b>	-0.042	-0.079	0.114
$\text{K}^+$	<b>0.830**</b>	1	-0.146	-0.159	0.124	-0.039	-0.115	0.109	0.049	0.122	0.115
$\text{Mg}^{2+}$	<b>0.776*</b>	0.540	1	<b>0.544**</b>	-0.034	<b>0.694**</b>	0.168	0.372	0.073	-0.010	0.263
$\text{Na}^+$	<b>0.916**</b>	<b>0.674*</b>	<b>0.897**</b>	1	0.381	<b>0.561**</b>	0.346	<b>0.476*</b>	0.070	-0.011	0.134
DOC	0.610	<b>0.698*</b>	0.177	0.449	1	-0.051	<b>0.560**</b>	<b>0.695**</b>	<b>0.706**</b>	<b>0.717**</b>	<b>0.635**</b>
$\text{NO}_3^-$	0.234	-0.112	<b>0.704*</b>	0.456	-0.153	1	0.278	0.391	0.074	-0.020	-0.068
$\text{NH}_4^+$	0.529	0.234	<b>0.704*</b>	<b>0.774*</b>	0.263	0.646	1	<b>0.866**</b>	<b>0.632**</b>	<b>0.666**</b>	<b>0.502*</b>
TN	0.502	0.276	0.614	<b>0.722*</b>	0.376	0.588	<b>0.960**</b>	1	<b>0.763**</b>	<b>0.747**</b>	<b>0.713**</b>
TP	0.487	0.385	0.484	0.589	0.531	0.478	<b>0.779*</b>	<b>0.910**</b>	1	<b>0.952**</b>	<b>0.720**</b>
PP	0.646	0.331	<b>0.766*</b>	<b>0.775*</b>	0.404	<b>0.777*</b>	<b>0.869**</b>	<b>0.884**</b>	<b>0.840**</b>	1	<b>0.675**</b>
DIP	<b>0.746*</b>	0.587	<b>0.736*</b>	<b>0.864**</b>	0.654	0.488	<b>0.865**</b>	<b>0.891**</b>	<b>0.838**</b>	<b>0.865**</b>	1

The right upper part and left lower part represent fish farming ponds and natural ponds, respectively. \*\*significant at the 0.01 level (two-tailed), \*significant at the 0.05 level (two-tailed).

In the natural ponds, the alkali elements were also positively correlated with dissolved inorganic phosphorus (DIP), like  $\text{Ca}^{2+}$ -DIP ( $r = 0.75$ ),  $\text{Mg}^{2+}$ -DIP ( $r = 0.74$ ) and  $\text{Na}^+$ -DIP ( $r = 0.86$ ), indicating the existence of alkali metal phosphates, for example  $\text{CaHPO}_4$ ,  $\text{Ca}(\text{H}_2\text{PO}_4)_2$  and  $\text{NaH}_2\text{PO}_4$ . These kinds of phosphate are common in the soil solutes, suggesting the terrestrial origins of alkali metals caused by the surface runoff to the natural ponds. In contrast, alkali elements did not show significant correlation with phosphorus in the fish farming ponds, like  $\text{Ca}^{2+}$ -DIP ( $r = 0.11$ ),  $\text{Mg}^{2+}$ -DIP ( $r = 0.26$ ) and  $\text{Na}^+$ -DIP ( $r = 0.13$ ). The significant positive correlation was observed between alkali metals and nitrogen components, like  $\text{Ca}^{2+}$ - $\text{NO}_3^-$  ( $r = 0.52$ ),  $\text{Mg}^{2+}$ - $\text{NO}_3^-$  ( $r = 0.69$ ) and  $\text{Na}^+$ - $\text{NO}_3^-$  ( $r = 0.48$ ), indicating the existence of nitrate of alkali metals. As previous studies indicated, the nitrogen in the fishponds was mainly derived from feeding stuff [8] [9]. Hence, the positive correlation of alkali metals and nitrogen in the fishponds suggested the influence of fishing practices on the geochemical behaviors of alkali metals.

### 3.2.2. Impacts of Land Use

Previous studies indicated that land use was an important factor of water chemistry [14]. For example, agricultural land led to increase in  $\text{K}^+$ , nitrogen and phosphorus. Rivers have higher  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$  nitrogen and phosphorus in residential and industrial areas. To study the influence of land use types on alkali elements, the correlation of alkali elements with N and P commenting the ponds without fish farming (Table 2). In residential area, the significant positive correlation was observed among  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  and  $\text{Na}^+$ , like  $\text{Ca}^{2+}$ - $\text{Na}^+$  ( $r = 0.78$ ) and  $\text{Mg}^{2+}$ - $\text{Na}^+$  ( $r = 0.66$ ), suggesting a common origin from domestic wastewater combined with the significantly high contents of  $\text{Ca}^{2+}$  and  $\text{Na}^+$  in residential area (Figure 2). In agricultural land, alkali metals showed weak correlation between each other, for example,  $\text{Ca}^{2+}$ - $\text{Mg}^{2+}$  ( $r = 0.37$ ),  $\text{Ca}^{2+}$ - $\text{Na}^+$  ( $r = 0.57$ ,  $p > 0.05$ ) and  $\text{K}^+$ - $\text{Na}^+$  ( $r = 0.08$ ). This suggested that the geochemical behavior of alkali metals might be altered by the agricultural activities like tillage, extensive usage of pesticides and fertilizers.

### 3.3. Suitability Assessment for Irrigation

The suitability of pond water for irrigation was assessed according to the three indexes of sodium absorption ratio (SAR), sodium percentage (Na%), magnesium hazard (MH), which were calculated as the following equations [20] [26]:

$$\text{SAR} = \frac{\text{Na}^+}{\sqrt{\frac{\text{Ca}^{2+} + \text{Mg}^{2+}}{2}}} \quad (1)$$

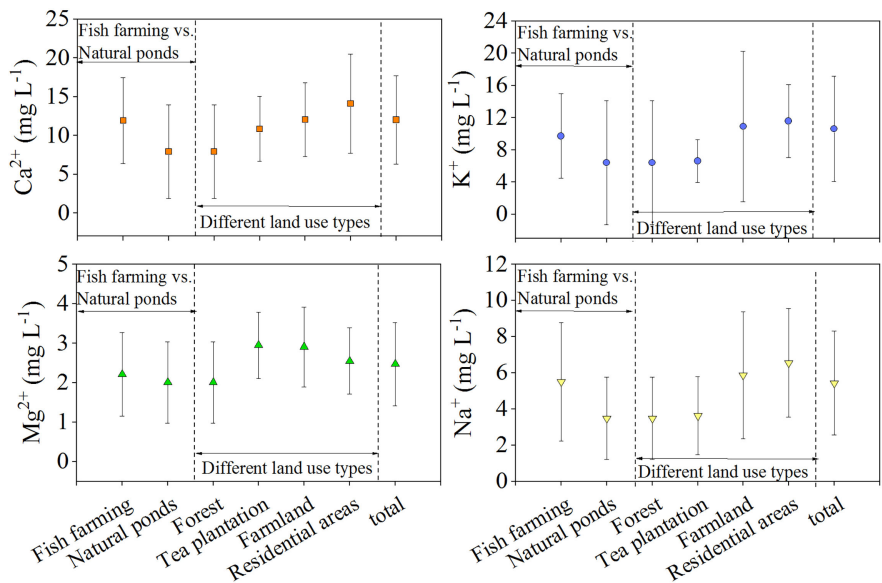
$$\text{Na}\% = \frac{(\text{Na}^+ + \text{K}^+) \times 100}{\text{Ca}^{2+} + \text{Mg}^{2+} + \text{Na}^+ + \text{K}^+} \quad (2)$$

$$\text{MH} = \frac{\text{Mg}^{2+} \times 100}{\text{Ca}^{2+} + \text{Mg}^{2+}} \quad (3)$$

**Table 2.** Pearson’s correlation coefficient between alkali elements and nutrient elements in the context of agricultural land and residential land.

	Ca <sup>2+</sup>	K <sup>+</sup>	Mg <sup>2+</sup>	Na <sup>+</sup>	DOC	NO <sub>3</sub> <sup>-</sup>	NH <sub>4</sub> <sup>+</sup>	TN	TP	PP	DIP
Ca <sup>2+</sup>	1	0.413	<b>0.722**</b>	<b>0.782**</b>	0.446	0.159	0.397	0.476	0.510	0.434	<b>0.617*</b>
K <sup>+</sup>	<b>0.726*</b>	1	0.386	0.544	0.217	-0.042	-0.007	0.119	-0.107	-0.150	-0.061
Mg <sup>2+</sup>	0.365	0.102	1	<b>0.659*</b>	0.239	<b>0.690**</b>	<b>0.598*</b>	<b>0.759**</b>	<b>0.650*</b>	<b>0.628*</b>	<b>0.732**</b>
Na <sup>+</sup>	0.572	0.078	0.004	1	0.533	0.346	0.403	<b>0.657*</b>	0.441	0.369	<b>0.572*</b>
DOC	0.576	0.215	<b>0.650*</b>	0.485	1	0.033	0.370	0.439	0.362	0.314	0.299
NO <sub>3</sub> <sup>-</sup>	-0.381	-0.253	0.202	-0.091	-0.154	1	0.474	<b>0.707**</b>	0.480	0.519	<b>0.562*</b>
NH <sub>4</sub> <sup>+</sup>	0.096	0.023	<b>0.706*</b>	-0.019	0.499	<b>0.648*</b>	1	<b>0.860**</b>	<b>0.952**</b>	<b>0.926**</b>	<b>0.906**</b>
TN	0.253	0.134	<b>0.750**</b>	0.082	<b>0.619*</b>	0.549	<b>0.967**</b>	1	<b>0.825**</b>	<b>0.779**</b>	<b>0.865**</b>
TP	-0.231	-0.064	<b>0.607*</b>	-0.362	0.202	<b>0.763**</b>	<b>0.872**</b>	<b>0.813**</b>	1	<b>0.986**</b>	<b>0.965**</b>
PP	0.066	0.165	<b>0.651*</b>	-0.179	0.404	<b>0.638*</b>	<b>0.941**</b>	<b>0.937**</b>	<b>0.911**</b>	1	<b>0.934**</b>
DIP	0.132	0.188	0.499	-0.081	0.148	<b>0.735**</b>	<b>0.860**</b>	<b>0.801**</b>	<b>0.764**</b>	<b>0.860**</b>	1

The right upper part and left lower part represent the ponds surrounded by residential and agricultural land, respectively.



**Figure 2.** Comparison of alkali metals concentrations in two different scenarios.

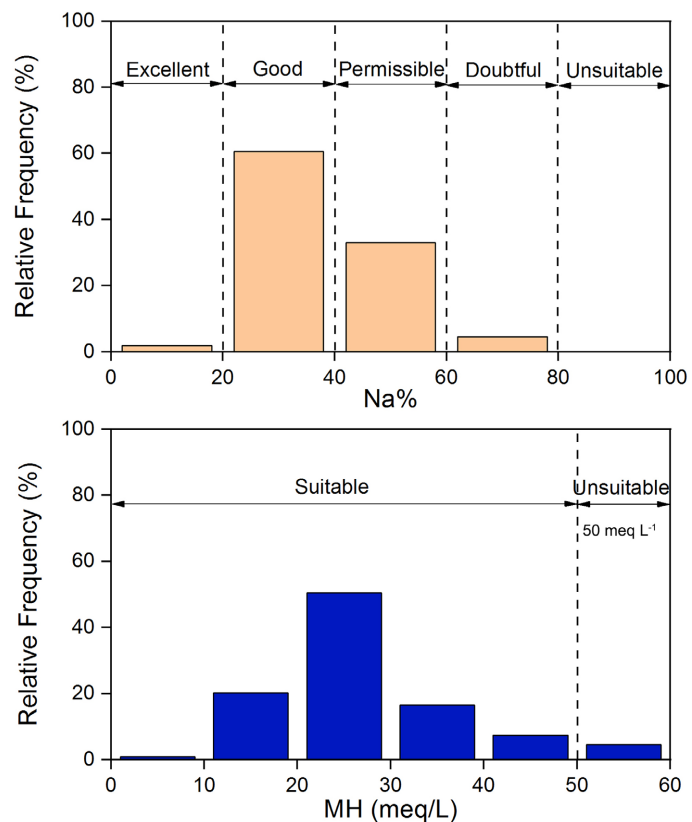
where the concentrations of alkali metals are expressed in meq·L<sup>-1</sup>.

High levels of Na<sup>+</sup> contents lead to displacement of Ca<sup>2+</sup> and Mg<sup>2+</sup> in soil and affect soil structure, aeration and infiltration, which will cause a drop of crop yield [21]. SAR accounts for the effects of Na<sup>+</sup> and is usually used as an assessment index of water quality for irrigation, with high levels of SAR affecting the growth and yield of crops [19] [20]. SAR can be classified into 3 categories as follows [20]: good (0 - 6 meq·L<sup>-1</sup>), doubtful (6 - 9 meq·L<sup>-1</sup>) and unsuitable (>9 meq·L<sup>-1</sup>). SAR in this study ranged from 0.08 to 0.87 meq·L<sup>-1</sup>, which is much lower than the reference value unsuitable for irrigation. This indicated that the

pond water was suitable for crops growth with respect to SAR.

Different from SAR, sodium percentage (Na%) incorporates the effects of  $\text{Na}^+$  and  $\text{K}^+$  since  $\text{K}^+$  is reported to affect the concentration of exchangeable  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  [27]. Na% can be classified into 5 categories as follows [26]: excellent (<20%), good (20% - 40%), permissible (40% - 60%), doubtful (60% - 80%) and unsuitable (>80%). Na% in this study varied from 13% to 78%, falling into the “Excellent” category to “Doubtful” category. In all, 38% of samples were marginally suitable for irrigation. Pond water in residential area had higher level of Na% than other land use types. Fishponds had higher Na% than those of natural ponds without fish.

The high levels of  $\text{Mg}^{2+}$  have adverse effect on soil hydraulic properties when  $\text{Mg}^{2+}$  is 50% larger than  $\text{Ca}^{2+}$  [19] [27]. MH can be classified into 2 categories as follows: suitable (<50  $\text{meq}\cdot\text{L}^{-1}$ ) and unsuitable (>50  $\text{meq}\cdot\text{L}^{-1}$ ). In this study area, MH of pond water ranged from 9.91 to 57.91  $\text{meq}\cdot\text{L}^{-1}$ , with 5% of samples falling into “Unsuitable” category (Figure 3). The highest MH value was located in ponds distributed in the tea plantation and forest land. Overall, most of the pond water is suitable for irrigation with respect to SAR, Na% and MH. However, some of ponds in residential area and tea gardens should be of concern when considering that ~40% of ponds were marginally suitable for irrigation in terms of Na% and ~5% of ponds was unsuitable in terms of MH.



**Figure 3.** Relative frequency of Na% and MH of pond water in the study catchment.



## 4. Conclusion

This study explored the impacts of fish farming and land use types on the contents of alkali (earth) metals ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^+$  and  $\text{Na}^+$ ) for pond and reservoir ecosystems in a subtropical agricultural watershed, China. In the context of forest land, the fishponds have higher contents of alkali (earth) metals than natural ponds without fish, but the difference is not significant as expected since quick lime and salt were used as disinfectants in fishponds. As for land use, the ponds and reservoirs in residential area have significantly higher  $\text{Ca}^{2+}$  and  $\text{Na}^+$  concentration than other land use types, reflecting the impact of domestic wastewater. The suitability of pond and reservoir water for irrigation was assessed using SAR, Na% and MH. Although most of pond and reservoir water bodies are suitable for irrigation, some pond water bodies in residential area and tea gardens should be paid attention since levels of Na% and MH were marginally suitable for irrigation.

## Fund

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## Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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