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ARTICLE

Quantification of the Kinetics of Soil Selenium Diffusive Gradients in Thin-Films Process under Long-Term Moisture Changes

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ABSTRACT

The effects of long-term moisture changes on the migration, release, and bioavailability of selenium in soil are complex. Due to the lack of effective monitoring methods for precise quantification, its dynamic behavior is still unclear. Based on the DGT (Diffusive Gradients in Thin-films) technology, this study sets up three moisture control scenarios: continuous wet, wet-dry alternating, and continuous dry, and carries out a 6-month soil moisture control experiment. In the experiment, the DGT device collected the diffusion gradient data of soil selenium under different scenarios, and analyzed the migration characteristics of selenium in combination with the adsorption isotherm. Meanwhile, the release rate, migration coefficient, and bioavailability parameters of selenium are calculated by fitting the first-order kinetic model, further verifying the reliability and applicability of the DGT data. The experimental results demonstrate that under continuous wet conditions, the release rate of soil selenium reaches 1.85 $\mu g \cdot cm^{-2} \cdot h^{-1}$, with a migration coefficient of 0.012 $cm^2 \cdot h^{-1}$ and a bioavailability parameter of 0.74; under wet-dry alternating conditions, they are 1.42 $\mu g \cdot cm^{-2} \cdot h^{-1}$, 0.01 $cm^2 \cdot h^{-1}$, and 0.68, respectively;

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under continuous dry conditions, the release rate of soil selenium is the smallest, at 0.88 $\mu g \cdot cm^{-2} \cdot h^{-1}$, with a migration coefficient of 0.004 $cm^2 \cdot h^{-1}$ and a bioavailability parameter of 0.5. The results of this experiment reveal the dynamic behavior of soil selenium under different moisture conditions and reflect the high efficiency of DGT technology in dynamic monitoring and quantitative analysis of soil selenium behavior, providing a scientific basis for the optimal management of rhizosphere soil selenium.

Keywords: Soil Selenium Dynamics; Moisture Regulation Effects; Diffusive Gradients in Thin-Films; Selenium Bioavailability Analysis; Kinetic Analysis

1. Introduction

Selenium in soil, as an essential trace element for the human body, plays a vital role in maintaining biological health and ecological balance in the environment. Selenium [1, 2] not only significantly promotes plant growth [3, 4], but also affects the health of animals and humans through the food chain. The behavior of selenium in soil [5, 6] is complex and changeable. It is affected by many factors, and its migration [7, 8], release, and bioavailability are difficult to accurately predict. In recent years, the dynamics of soil moisture conditions [9, 10] has gradually become an important factor influencing the behavior of selenium [11, 12] with changes in agricultural production activities and environmental conditions. Long-term moisture changes can significantly change the morphological distribution [13, 14] and migration mechanism of selenium in soil. However, most existing studies focus on the behavioral characteristics of selenium under static conditions, and lack in-depth discussion on the release [15, 16] and migration rules of selenium under dynamic moisture changes. Due to the strong spatiotemporal heterogeneity of selenium in environmental behavior [17, 18], traditional monitoring and analysis methods [19, 20] cannot meet the requirements of studying the migration and bioavailability of selenium under dynamic conditions, and the impact of long-term moisture changes on soil selenium is still unclear. This limitation of understanding has hindered the rational use of selenium in agriculture and environmental management, and has also brought challenges to the assessment of the ecological risks of soil selenium and the formulation of relevant management strategies. Therefore, research on the behavior of soil selenium under dynamic moisture conditions, especially the development of effective monitoring and quantification methods, has important scientific value and practical significance.

In recent years, as an important trace element in soil, the migration behavior, release process and bioavailability of selenium have gradually attracted widespread attention. Zhang, Chen and Zhong [21] systematically studied the migration characteristics of effective selenium in soil under drip irrigation conditions by combining field experiments with indoor simulation methods, and revealed the key influence of drip irrigation amount and soil type on selenium migration and distribution, providing a theoretical basis for optimizing selenium nutrition management and precision drip irrigation technology. It is worth noting that the migration and distribution characteristics of selenium in the soil-plant [22, 23] system are not only closely related to external environmental factors, but also regulated by complex processes at the soil-plant interface. Zhong, Zhang and Tao [24] studied the application of chemical extraction, DGT, isotope tracing, and other research methods in the migration and transformation of selenium in the soil-plant system, pointed out that the migration and transformation of selenium are affected by the coupling of multiple factors, and emphasized the importance of strengthening the study of selenium migration, transformation, and enrichment in plants. As a key environmental variable, moisture dynamic changes have a profound impact on the morphological evolution and migration path of selenium in soil [25, 26]. Song, Liu and Cui [27] analyzed the changes in soil selenium forms over time during flood irrigation and their relationship with changes in soil physical and chemical properties through indoor simulation experiments and explored the migration characteristics of selenium in soil. Finally, they put forward suggestions for the development of selenium-rich agriculture and found that flood irrigation accelerates the loss of soil selenium and reduces its bioavailability. Although the above research has made important progress, the current research on the comprehensive effects of different irrigation methods and coupled environmental factors on selenium migration, transformation, and bioavailability [28, 29] is still insufficient, especially in the quantitative analysis on a long time scale.

DGT is a technology used to dynamically monitor the concentration gradient of elements in a solution. It captures the diffusion behavior of the target substance through a thin film diffusion layer, thereby providing data with high temporal and spatial resolution. This technology is widely used in the field of environmental science, especially in the quantitative analysis of heavy metals and nutrients in soil and water. Compared with traditional monitoring methods, DGT shows higher sensitivity and accuracy in dealing with dynamic changes under complex environmental conditions. Wei et al. [30] discussed the development history, research hotspots, and trends of DGT technology, and emphasized the technological development and practical application potential of DGT in environmental science research. The principle and flexibility of DGT technology [31, 32] enable it to adapt to the detection needs of various targets in different environmental media, thus showing broad application prospects in the field of environmental monitoring. Pantoja and Garelick [33] discussed the methods of using DGT technology to quantify, analyze, and detect radionuclides in the environment and pointed out its insights in understanding the behavior of radionuclides, method development, practical applications, advantages, limitations, and future prospects. The interdisciplinary integration of technical means has gradually become an important direction to enhance the depth and breadth of DGT applications. Xu et al. [34] combined DGT technology with SERS (Surface-Enhanced Raman Spectroscopy) technology and used specific nanostructure design to achieve rapid, ultra-sensitive detection and imaging of arsenic forms in the environment, revealing the spatial distribution characteristics of arsenic at the sediment-water interface. These studies have demonstrated the great potential of DGT technology in different fields, but existing work has not fully solved the limitations of technology applications. Further research is needed on the simultaneous detection capability and stability of multiple elements in complex environments.

To solve this problem, this paper designs a series of long-term moisture regulation experiments based on DGT technology to explore the dynamic behavior of soil selenium under three typical moisture conditions: continuous wet, wet-dry alternating, and continuous dry. First, representative soil samples are collected, and different moisture scenarios are set after pretreatment. The experimental conditions are precisely controlled to simulate the effects of long-term moisture changes on the migration and release of soil selenium. In the experiment, the DGT device is used to collect the diffusion gradient data of selenium in the soil solution, and the migration characteristics and release mechanism of selenium under different moisture scenarios are systematically analyzed in combination with adsorption isotherm determination and kinetic analysis. To further quantify the kinetic parameters of selenium, the first-order kinetic model is used to fit the release rate and migration coefficient of selenium, and the bioavailability parameters are calculated to reveal the bioavailability potential of selenium under different scenarios. By comparing the results of DGT technology with those of traditional chemical extraction methods, the reliability and efficiency of DGT technology in dynamic monitoring of soil selenium behavior are fully verified. This study achieves the dynamic monitoring and quantification of soil selenium migration and release processes in terms of method, providing a new tool for in-depth understanding of the impact of moisture changes on selenium behavior. At the application level, the study reveals the dynamic characteristics and laws of selenium under different moisture conditions, providing a scientific basis for improving soil management and the rational use of selenium resources. This study not only fills the gap in the study of soil selenium behavior under dynamic moisture conditions, but also provides ideas and methods for future similar studies.

2. Long-Term Moisture Regulation and Selenium Behavior Monitoring Methods

2.1. Soil Sample Collection and Pretreatment

Soil sample collection is carried out strictly according to the plan in the early stage of the experiment to ensure that the samples are well representative and consistent. The sampling site is selected from a typical agricultural area with stable land use, where rice and wheat are rotated for a long time, and the soil type is yellow-brown soil. Yellow-brown soil is a typical soil type widely distributed in temperate and subtropical regions, and is common in areas with humid climates and moderate precipitation. This soil is formed in an environment where organic matter accumulates slowly, and usually has good drainage and air permeability under natural conditions. The parent material of yellow-brown soil is usually weathered rock or minerals with high iron and aluminum content. The soil color is yellow-brown or yellow-brown, mainly formed by the accumulation of iron and aluminum oxides. The soil structure is relatively loose, the texture is light, and it is rich in elements such as iron and aluminum, but lacks elements such as calcium and phosphorus, so its fertility is relatively medium. Yellow-brown soil usually has a good water retention capacity in agricultural production, but it is highly acidic and easily affected by acidification, and reasonable fertilization is required to maintain good soil production performance. The sampling adopts a stratified sampling method, with a depth set to 0–20 cm, and sampling points are evenly distributed in the experimental area. About 1 kg of soil is collected at each sampling point and combined into a mixed sample to reduce the accidental deviation of a single sampling point. Each mixed sample is prepared by mixing soil from 5 random sampling points in the same area, and a total of 5 mixed samples are obtained, numbered S1 to S5. The sampling diagram is shown in **Figure 1**.

Figure 1. Soil sampling map.

The collected soil samples are placed in clean polyethylene sealed bags, marked with the sampling time, location and sample number, and quickly transported to the laboratory. To prevent the samples from getting damp or contaminated during transportation, all samples are tightly sealed. After arriving at the laboratory, the samples are naturally air-dried in a clean environment, avoiding direct sunlight and contact with external pollutants during the process. The air-dried soil samples are sieved with a stainless steel sieve with a pore size of 2 mm to remove impurities such as stones and plant residues to ensure sample homogenization. The sieved samples are evenly spread on a clean workbench, and the samples are divided into four equal parts. Two of them are randomly selected and combined and spread evenly again. The above operation is repeated until the sample volume is about 50 g. The final selected samples are finely ground using an agate mortar until all particles pass through a 100-mesh sieve to ensure that the sample particles are uniform and fine. The ground samples are placed in a clean small sealed bag and labeled for physical and chemical analysis. The remaining parts are sealed and stored in a desiccator for further experiments.

The physical and chemical properties analysis of soil samples includes the determination of pH, organic matter content, total selenium content, and soluble selenium content, and the soil texture is classified. The relevant information and analysis results of each sample are detailed in **Table 1**.

Table 1. Basic physical and chemical properties and sampling point information of different soil samples.

Sample ID	Number of Sampling Points	Organic Matter Content (%)	Total Selenium Content (mg kg^{-1})	Soluble Selenium Content (mg kg^{-1})	pH Value	Soil Texture
S1	5	2.3	0.45	0.12	6.8	Loam
S2	5	2.1	0.5	0.15	6.5	Loam
S3	5	2	0.47	0.13	6.7	Clay loam
S4	5	1.9	0.44	0.1	6.9	Loam
S5	5	2.2	0.46	0.11	6.6	Loam

The entire sampling and pretreatment process is strictly carried out in accordance with the relevant standard procedures for soil analysis to ensure sample quality and the repeatability and reliability of the experiment.

2.2. Design of Long-Term Moisture Regulation Experiment

When studying the migration and release characteristics of soil selenium under different moisture conditions, the experiment designs three typical moisture scenarios: continuous wet, wet-dry alternating, and continuous dry, and precisely controls conditions such as humidity, temperature, and experimental duration. The continuous wet scenario maintains soil moisture at 85%–90% of the field water holding capacity through periodic irrigation to simulate the dynamic behavior of soil selenium under long-term wet conditions. The experiment lasts for 180 days, and the temperature is set to 25 °C. The wet-dry alternating scenario is based on a 10-day cycle. In the first 7 days, the soil moisture is adjusted to 80% of the field water holding capacity through irrigation, and the soil is allowed to evaporate naturally to 30%–40% in the last 3 days to simulate the seasonal moisture fluctuation environment. The experiment also lasts for 180 days, and the temperature is set to 25 °C. In the case of continuous dry, irrigation is stopped, and soil moisture naturally decreases and maintains at 10%–15% of field water holding capacity, simulating the dynamic change behavior of soil selenium in a long-term drought environment. The temperature is also set to 25 °C, and the duration is 180 days. During the entire experiment, the data changes of key parameters are quantitatively monitored to analyze the effects of different moisture conditions on the migration and release of selenium. **Table 2** shows the main parameters monitored in the experiment and related information.

Table 2. Monitoring parameters during the experiment.

Parameter	Measurement Range	Accuracy	Measurement Frequency
Moisture	0–100%	±0.1%	Daily
Temperature	–10∼50 ℃	±0.5 ℃	Daily
Selenium concentration	0.1–10 mg L^{-1}	±0.01 mg L^{-1}	Every 10 days
pH value	4–9	±0.05	Every 15 days

To ensure the consistency and repeatability of experimental conditions, moisture control under wet and dry conditions is achieved through quantitative irrigation and real-time monitoring of soil moisture sensors. The determination of the humidity range is based on the measured value of the maximum water holding capacity of the soil, and is dynamically regulated according to the experimental needs of different scenarios. The moisture control of wet-dry alternating conditions adopts the method of staged irrigation and natural evaporation, and the soil moisture changes within the target range by adjusting the irrigation amount and air drying time. The temperature is controlled by a constant temperature incubator and kept constant throughout the experimental stage to eliminate the interference of temperature changes on the migration and release of soil selenium. To improve the accuracy and scientificity of the experiment, three parallel repetitions are set for each moisture scenario, and the moisture, selenium content, and physical and chemical properties of soil samples are measured regularly to ensure the stability and reliability of the data.

2.3. DGT Device Operation and Data Acquisition

The working principle of the DGT device is based on the law of diffusion of substances in thin-films. The target substance is captured within a certain period of time through a prefabricated gel membrane, and the concentration change of the captured substance is analyzed to infer its diffusion gradient and mobility in the environmental medium. The core of the device consists of three parts: a diffusion layer, a binding layer, and a protective film. Among them, the thickness of the diffusion layer determines the diffusion path and speed of the target substance; the binding layer is responsible for accommodating the adsorbent to capture the target substance; the protective film is used to prevent external interference and ensure the uniformity of diffusion. When assembling the device, it is necessary to ensure that there is no overlap of bubbles between the diffusion layer and the binding layer to avoid uneven diffusion paths. After assembly, it is fixed by a bracket to make it in close contact with the protective film, ensuring that the protective film is in full contact with the soil surface during the experiment to avoid air isolation affecting the diffusion process. During the experiment, the device needs to be fixed in a stable environment to reduce the impact of vibration on diffusion.

The time node of data collection is set to multiple samplings at a certain interval based on the migration characteristics of the target substance and research needs. After each sampling, the gel layer on the surface of the device is cleaned and separated, and the concentration of the target substance in the binding layer is determined using a spectrophotometer or other analytical instrument. According to the concentration change of the target substance and the thickness of the diffusion layer, the diffusion flux J and concentration gradient C are calculated, and the formulas are:

$$J = {}^{M}\Big/_{A \cdot t} \tag{1}$$

$$C = {}^{J \cdot \Delta g}\Big/_{D} \tag{2}$$

Among them, M is the total amount of target substance captured by the binding layer within time t; A is the cross-sectional area of the diffusion layer; Δg is the thickness of the diffusion layer; D is the diffusion coefficient of the target substance in the diffusion layer.

During the measurement of the diffusion gradient, it is necessary to ensure the tightness of the device and the constancy of the experimental conditions to avoid interference of external factors on the diffusion behavior of the target substance. By repeating the experiment and comparing the data, the stability and reliability of the results are confirmed, providing an accurate basis for the dynamic monitoring and quantitative analysis of soil target substances.

2.4. Selenium Migration and Release Kinetics

The migration and release process of soil selenium is affected by moisture conditions and has differences in moisture situations. To study the migration and release mechanism of selenium, the selenium release characteristics under different moisture conditions are analyzed by combining the adsorption isotherm method. The migration of selenium in soil is mainly carried out through two mechanisms: diffusion and adsorption. In the soil, selenium ions diffuse to the film interface of the DGT device through moisture and interact with the adsorption sites on the surface of soil particles. The adsorption capacity and moisture conditions of the soil surface have an important influence on the migration and release characteristics of selenium, which need to be further analyzed through adsorption isotherm experiments. The adsorption isotherm can be fitted by the Langmuir or Freundlich model. The Langmuir model assumes that the soil surface is a uniform adsorption site and the adsorption reaction is a monolayer adsorption. Its expression is:

$$q_e = {}^{q_m K_L C_e}\Big/_{1 + K_L C_e} \tag{3}$$

Among them, q_e is the concentration of selenium adsorbed on a unit mass of soil; C_e is the concentration of selenium in the equilibrium solution; q_m is the maximum adsorption amount; K_L is the Langmuir constant. This model can effectively describe the saturation of the adsorption sites on the soil surface and the affinity of the adsorbent.

The Freundlich adsorption isotherm model is suitable for the case of uneven surface adsorption. Its expression is:

$$q_e = K_f C_e^{1/n} \tag{4}$$

Among them, K_f is the Freundlich constant, representing the adsorption capacity, and $1/n$ is the exponent of the adsorption intensity. This model is used to describe the multi-point adsorption of selenium in the soil.

This paper selects the Langmuir adsorption isotherm model to describe the adsorption behavior of selenium in soil. According to the assumption of the Langmuir model, the soil surface has uniform adsorption sites. Each adsorption site can only adsorb one selenium molecule, and the adsorption is reversible. This model is suitable for the situation where the adsorption sites on the soil surface are relatively uniform, and can more fully reflect the adsorption characteristics of selenium in the soil. The Langmuir model is chosen because the soil often shows strong saturation during the adsorption process. Under different moisture conditions, the saturation time of the adsorption sites on the soil surface is relatively early, indicating that the adsorption process is most consistent with the Langmuir hypothesis. As an alternative model, the Freundlich adsorption isotherm model is also fitted. The Freundlich model is suitable for describing soils with heterogeneous adsorption sites, but its applicability is not as good as the Langmuir model, and the model fit is low at high selenium concentrations. Therefore, the Langmuir model is finally selected to quantitatively describe the adsorption behavior of selenium in soil.

The dynamic changes of selenium release rate and migration coefficient are fitted by the first-order kinetic model [35]. The first-order kinetic model is often used to describe the release process of a substance, especially the migration behavior at the soil-solution interface. Its basic form is:

$$dC/dt = -kC \tag{5}$$

Among them, C is the concentration of selenium in the soil; t is time; k is the release rate constant. By logarithmically transforming the experimental data, a linear relationship is obtained:

$$\ln(C(t)) = \ln(C_0) - kt \tag{6}$$

According to the regression analysis results, the release rate constant k is fitted, and the release rate is calculated:

$$R = kC_0 \tag{7}$$

The migration coefficient of selenium in the experiment is calculated by the diffusion gradient data of the DGT device [36]. The basic principle of DGT is based on the control of solute diffusion, and there is a direct relationship between its migration coefficient and diffusion gradient:

$$D = \Delta C/\Delta t \times \delta/C_0 - C_s \tag{8}$$

Among them, ΔC is the concentration change in the diffusion layer; Δt is the experimental time; δ is the thickness of the diffusion layer; C_0 is the initial concentration; C_s is the surface concentration. The selenium diffusion gradient data recorded by the DGT device are processed to further calculate the migration coefficient of selenium in the soil, thereby revealing the migration rate and diffusion characteristics of selenium under different moisture conditions.

To quantify the bioavailability of selenium in soil, the study also adopts a method to calculate the bioavailability parameter. BEP (Bioavailability Evaluation Parameter) is used to evaluate the potential of an element for plant absorption and is defined as:

$$BEP = C_{\text{DGT}}/C_{\text{total}} \tag{9}$$

Among them, C_{DGT} is the element concentration measured by the DGT device, and C_{total} is the total selenium concentration in the soil. The larger the BEP value, the higher the bioavailability of selenium in the soil to plants. Under different moisture conditions, the change in BEP value reflects the availability of selenium in the soil and its impact on plants.

This study combines adsorption isotherm analysis, first-order kinetic model fitting, and bioavailability parameter calculation to comprehensively study the migration and release behavior of selenium in soil under different moisture conditions, and at the same time provide a quantitative analysis method for its dynamic process in soil.

2.5. Data Processing and Statistical Analysis Methods

The data obtained by DGT is processed to ensure their accuracy and reliability. First, the raw data is cleaned to remove abnormal data caused by operational errors, device failures, or changes in the external environment. There must be a control group so that multiple experiments can be carried out under different conditions to ensure the repeatability of the data obtained under different conditions. To ensure the stability and reliability of the data in each experimental cycle, three parallel experiments are carried out on the DGT device in each case. All experimental data are fitted using the least squares method to calculate the diffusion flux and concentration gradient of selenium under different moisture conditions. Then, data normalization normalizes the measured values to eliminate the influence of inherent differences between samples as much as possible. The standard formula for normalization is:

$$Z = X - \mu/\sigma \tag{10}$$

Among them, Z is the standardized data; X is the original data; μ and σ are the mean and standard deviation of the data, respectively. This processing step eliminates the scale differences between different experimental groups and facilitates direct comparison of data under different moisture scenarios. The data before and after normalization are shown in **Figure 2**.

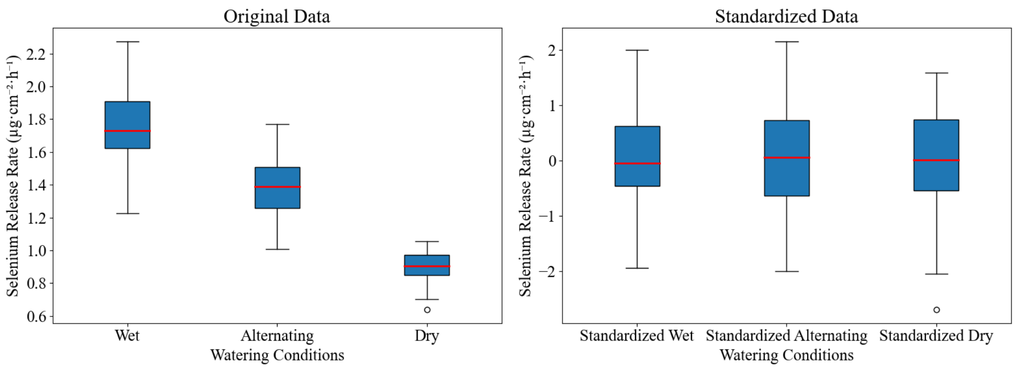

Figure 2. Standardization of selenium release rate under different moisture conditions.

The standardization process removes the scale difference, making the data under different moisture conditions comparable, and facilitating a more intuitive assessment of the impact of each condition on selenium release behavior.

During the data analysis process, the analysis of variance (ANOVA) is used to perform statistical tests on the selenium release rate, migration coefficient, and bioavailability parameters under different moisture conditions to determine whether the differences in selenium behavior under different moisture conditions are statistically significant. The specific test formula is:

$$F = {}^{MS_{\mathrm{be}}}\Big/_{MS_{\mathrm{w}}} \tag{11}$$

Among them, MS_{be} is the mean square between groups; MS_{w} is the mean square within groups; F is the F value, which is used to measure the significance of the difference between groups. If the F value is significantly higher than the critical value, it means that there is a significant difference in selenium behavior under different conditions. The F value is calculated by comparing the variance between and within groups to evaluate the differences between experimental groups. To further verify the reliability of the results, the data under each moisture scenario are tested for repeatability, and regression analysis is used to fit the experimental data. The R^2 value is used to evaluate the goodness of model fit. The calculation formula for the goodness of fit R^2 is:

$$R^2 = 1 - {}^{\sum_{i=1}^{n} (y_i - \hat{y}_i)^2}\Big/_{\sum_{i=1}^{n} (y_i - \bar{y})^2} \tag{12}$$

Among them, y_i and $\bar{y}$ are the observed value and its mean, respectively, and $\hat{y}_i$ is the fitted value. The closer the R^2 value is to 1, the better the fit effect and the higher the reliability of the results.

All statistical data are analyzed and processed using R language software. A two-sided test method is used, and the significance level is set to 0.05. The error analysis in the experimental results includes the calculation of the standard error and the estimation of the 95% confidence interval to ensure the credibility and robustness of the conclusions. In the experiment, the data differences between repeated experiments are evaluated by the standard deviation and the coefficient of variation. The calculation formula for the coefficient of variation is:

$$CV = {}^{\sigma}\Big/_{\mu} \times 100\% \tag{13}$$

CV value is used to measure the stability and consistency of experimental data. Smaller CV value indicates lower variability of data and higher reliability of experimental results. All data have been strictly statistically processed and analyzed to ensure that the experimental conclusions are scientific and credible.

3. Results

3.1. Changes in Soil Selenium Release Rate under Different Moisture Conditions

This paper deeply explores the effects of moisture changes on soil selenium migration and bioavailability through the release characteristics of soil selenium under different moisture scenarios. The experiment regularly monitors the changes in selenium release rate under three moisture conditions: continuous wet, wet-dry alternating, and continuous dry, and captures the dynamic behavior of selenium in soil through DGT technology. The regulatory effect of moisture changes on selenium release is revealed through data collection and analysis. **Figure 3** shows the trend of soil selenium release rate over time under various moisture scenarios in the experiment.

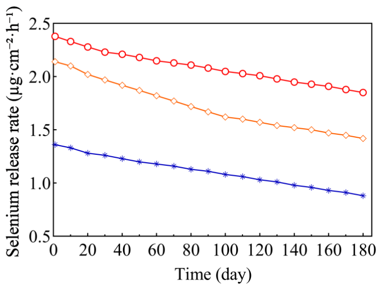

Figure 3. Changes in soil selenium release rate under different moisture conditions.

Figure 3 shows that under continuous wet conditions, the release rate of soil selenium always remains at a high level, gradually stabilizing from the initial 2.38 $\mu g \cdot cm^{-2} \cdot h^{-1}$ and dropping to 1.85 $\mu g \cdot cm^{-2} \cdot h^{-1}$ at 180 days. This shows that under long-term wet conditions, the selenium release rate remains relatively stable. Although it has slightly decreased, the release rate tends to balance under sufficient moisture. Under wet-dry alternating conditions, the selenium release rate starts at 2.14 $\mu g \cdot cm^{-2} \cdot h^{-1}$ and gradually decreases to 1.42 $\mu g \cdot cm^{-2} \cdot h^{-1}$. This change reflects the dynamic regulation of moisture fluctuations on the migration and availability of soil selenium. Under continuous dry conditions, the selenium release rate is significantly lower than that under other conditions and remains at a low level, decreasing from the initial 1.36 $\mu g \cdot cm^{-2} \cdot h^{-1}$ to 0.88 $\mu g \cdot cm^{-2} \cdot h^{-1}$, indicating that moisture shortage severely restricts the release of selenium. The experimental results reveal the profound impact of moisture changes on the dynamic behavior of soil selenium. The higher selenium release rate under continuous wet conditions is in sharp contrast to the inhibitory effect under continuous dry conditions.

3.2. Time Series Changes in Soil Selenium Migration Coefficient

In soil ecological research, moisture conditions have a significant impact on the migration behavior of heavy metals and trace elements in soil. As an important trace element, the migration behavior of selenium in soil is affected by many factors, and moisture changes are particularly critical. The experiment simulates different moisture conditions, observes the migration characteristics of selenium in soil, and uses the migration coefficient D as an indicator to explore the dynamic changes of soil selenium under wet, wet-dry alternating, and dry conditions. As a key parameter to measure the migration ability of elements, the migration coefficient D provides quantitative data support for a deep understanding of the migration behavior of soil selenium through the combination of long-term experiments and DGT technology. **Figure 4** shows the changes.

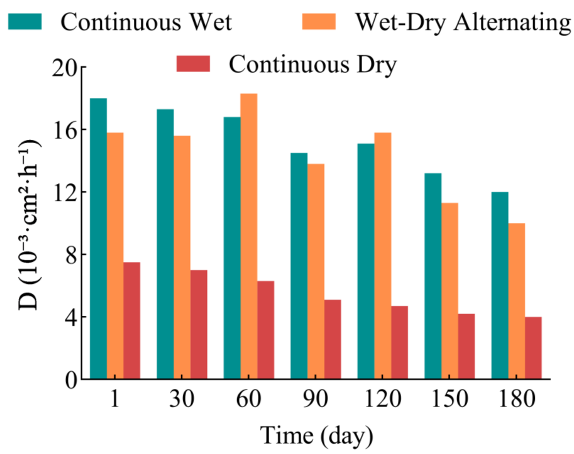

Figure 4. Time series changes of soil selenium migration coefficient under different moisture conditions.

As shown in **Figure 4**, under continuous wet conditions, the migration coefficient D gradually decreases from 18.0 $\times$ $10^{-3} \cdot cm^2 \cdot h^{-1}$ on day 1 to 12.0 $\times$ $10^{-3} \cdot cm^2 \cdot h^{-1}$ on day 180, indicating that under sufficient moisture conditions, the migration capacity of selenium gradually decreases over time, which is related to the equilibrium changes in the adsorption and desorption processes of selenium in the soil. Under wet-dry alternating conditions, the migration coefficient D shows large fluctuations, reaching 18.3 $\times$ $10^{-3} \cdot cm^2 \cdot h^{-1}$ on day 60, and then decreases to 10.0 $\times$ $10^{-3} \cdot cm^2 \cdot h^{-1}$ on day 180, indicating that the changes in soil structure caused by wet-dry alternating have a more complex effect on the migration of selenium. Under continuous dry conditions, the migration coefficient D continues to decrease from 7.5 $\times$ $10^{-3} \cdot cm^2 \cdot h^{-1}$ to 4.0 $\times$ $10^{-3} \cdot cm^2 \cdot h^{-1}$, reflecting that dry conditions significantly inhibit the migration capacity of selenium, and water deficiency leads to a significant decrease in the availability and migration capacity of selenium in the soil. The experimental results show that moisture conditions have an important influence on soil selenium migration. Selenium migration is relatively stable under moist conditions, while dry and wet-dry alternating conditions significantly inhibit the migration process.

3.3. Dynamic Changes in Bioavailability Parameters

In the experiment of long-term moisture changes, the influence of different wet conditions on the dynamic behavior of soil selenium is revealed by monitoring the soil selenium bioavailability parameter BEP under different moisture conditions. The experimental design systematically observes the bioavailability of soil selenium for 6 months by comparing three moisture management modes: continuous wet, wet-dry alternating, and continuous dry. The impact of changes in moisture conditions on soil selenium is evaluated by regular sampling and calculating the monthly BEP values. **Figure 5** shows the changes in BEP values each month under different moisture conditions, reflecting this dynamic process.

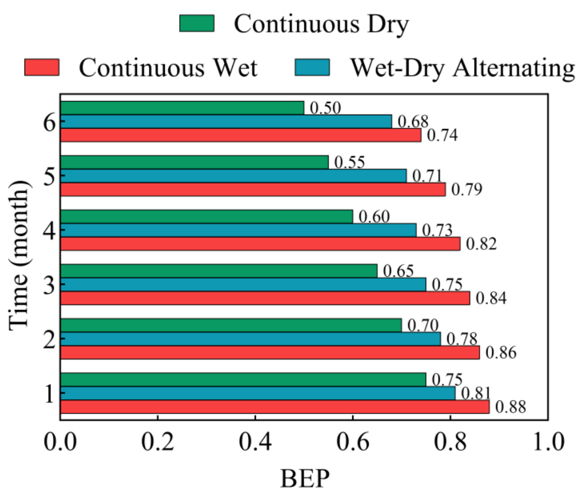

Figure 5. Changes in soil selenium bioavailability under moisture conditions.

As can be seen from the data in **Figure 5**, during the 6-month experiment, the BEP value under continuous wet conditions remains at a high level, gradually decreasing from 0.88 in the first month to 0.74 in the sixth month. In contrast, the BEP value under wet-dry alternating conditions shows a relatively stable downward trend, from 0.81 in the first month to 0.68 in the sixth month, while the BEP value under continuous dry conditions changes most significantly, with an initial value of 0.75, but drops to 0.50 in the sixth month. These changes indicate that under continuous wet conditions, selenium in the soil can maintain a high bioavailability, while wet-dry alternating conditions and continuous dry conditions lead to a gradual decrease in selenium bioavailability. The changes in selenium behavior under different moisture conditions reflect the key role of water supply in the availability of selenium in the soil, and the continuous supply of water has an important influence on maintaining the bioavailability of selenium.

3.4. Adsorption Isotherm Fitting Results and Migration Characteristics of Selenium

The adsorption and desorption behavior of soil selenium is significantly affected by moisture conditions. To quantitatively analyze the adsorption characteristics of selenium under different moisture conditions, this paper fits the experimental data based on the Langmuir adsorption isotherm model. Through the relationship between equilibrium concentration and adsorption amount, the differences in the migration characteristics and adsorption capacity of selenium under continuous wet, wet-dry alternating, and continuous dry conditions are clarified, revealing the dynamic adsorption law of selenium in soil. **Figure 6** shows the adsorption isotherms and fitting results under three moisture conditions, reflecting the adsorption kinetics of selenium in different moisture environments.

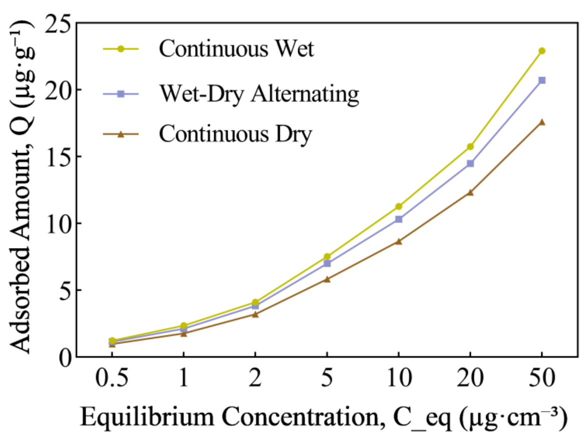

Figure 6. Fitting diagram of adsorption isotherms of soil selenium under different moisture conditions.

Under continuous wet conditions, the adsorption amount of selenium increases rapidly with the increase of equilibrium concentration and tends to saturation, which is related to the increase in the activity of adsorption sites on the soil surface when the moisture is sufficient. The adsorption amount is the largest, and the saturated adsorption amount reaches 22.93 $\mu g \cdot g^{-1}$. Under wet-dry alternating conditions, the growth rate of adsorption is slower than that in the wet condition, and the saturated adsorption amount is slightly lower, at 20.71 $\mu g \cdot g^{-1}$. This difference is related to the partial inactivation of adsorption sites or intermittent occupation of adsorption sites due to moisture fluctuations. Under continuous dry conditions, the adsorption amount increases most slowly, and the saturated adsorption amount is the lowest, only 17.61 $\mu g \cdot g^{-1}$, reflecting the weakening of soil adsorption capacity due to long-term drought. Overall, the goodness of fit of the adsorption isotherm is high, and the parameter differences indicate that the moisture conditions significantly affect the adsorption behavior of selenium by regulating the soil pore moisture dynamics and adsorption site activity. These characteristics provide a scientific basis for a deeper understanding of the law of soil selenium migration.

3.5. Comparison between DGT Technology and Traditional Methods

This section explores three different monitoring methods by comparing and analyzing the migration and release characteristics of soil selenium under different moisture conditions: DGT technology, chemical extraction method, and electrochemical sensor method. These methods have their own advantages and limitations in the application of dynamic monitoring of soil selenium, which are specifically manifested in the different ways and accuracy of data acquisition. DGT technology uses a thin-film diffusion gradient device to collect the dynamic situation of the concentration gradient of the target substance in real-time with high temporal and spatial resolution. The chemical extraction method extracts soluble selenium from the soil through various solvents. Although the method is relatively simple, it has certain limitations in terms of dynamics and accuracy. The electrochemical sensor method relies on electrochemical reactions to monitor changes in element concentrations in the soil. It has strong real-time performance, but its applicability is limited by the selectivity and stability of the sensor. If the release and migration performance of selenium in different moisture conditions is compared, combined with the measurement results of each method, the performance comparison of each environment is described in subsequent research, as shown in **Table 3**.

Table 3. Comparison of different methods under different moisture conditions.

Moisture Condition	Method	Release Rate ($\mu g \cdot cm^{-2} \cdot h^{-1}$)	Migration Coefficient ($cm^2 \cdot h^{-1}$)	Bioavailability Parameter (BEP)	Duncan Letter
Continuous wet	DGT technology	1.85	0.012	0.74	A
	Chemical extraction	1.9	0.015	0.72	A
	Electrochemical sensor	1.8	0.013	0.73	A
Wet-dry alternating	DGT technology	1.42	0.01	0.68	B
	Chemical extraction	1.35	0.008	0.65	B
	Electrochemical sensor	1.4	0.009	0.66	B
Continuous dry	DGT technology	0.88	0.004	0.5	C
	Chemical extraction	0.76	0.002	0.36	C
	Electrochemical sensor	0.82	0.003	0.42	C

As can be seen from **Table 3**, under continuous wet conditions, the release rate and migration coefficient of the chemical extraction method are the highest, which are 1.9 $\mu g \cdot cm^{-2} \cdot h^{-1}$ and 0.015 $cm^2 \cdot h^{-1}$, respectively. This shows that the stronger the dissolution effect of the chemical extraction method, the more complete the release of soluble selenium in the soil, and the higher the release rate and migration coefficient. Under wet-dry alternating and continuous dry conditions, the DGT technology performs best because it can well capture the diffusion gradient of trace elements in the soil and adapt to the dynamic release and migration behavior of selenium under different moisture changes. In general, DGT technology has higher applicability and reliability in the dynamic monitoring and quantitative analysis of selenium migration behavior in soil. In the analysis of Duncan's letter method, A, B, and C represent significant differences between different groups. The same letters indicate that there are no statistically significant differences between the groups, while different letters indicate that there are significant differences between the groups. Therefore, the numerical differences between the conditions represented by Group A and Group B or Group C are statistically significant, reflecting the degree of influence of different humidity conditions on the behavior of soil selenium. The results of the Duncan letter method showed that the three methods under continuous moist conditions had significantly higher values in release rate, migration coefficient, and bioavailability parameters, while the values under wet-dry alternating and continuous drying conditions were significantly lower, reflecting the promotion of these indicators by a moist environment.

4. Discussion

In the study of the behavior of selenium in soil and its dynamic changes, the contributions of predecessors cannot be ignored. Early studies revealed the key role of selenium in promoting plant growth and affecting animal and human health through the food chain. The effects of irrigation methods coupled with environmental factors on the migration, transformation and bioavailability of selenium have become the focus of attention. There is still a lack of in-depth understanding of the impact of long-term water changes on the release and migration of soil selenium, especially the technical difficulties of monitoring and quantitative analysis under dynamic conditions have not been fully resolved. This study used DGT technology to explore the dynamic behavior of soil selenium under three typical water conditions and provided detailed data support. The results showed that under continuous wet conditions, the release rate and migration coefficient of soil selenium were the highest. Adequate water promoted the transfer of selenium from the solid phase to the liquid phase, thereby enhancing its bioavailability. Under alternating dry-wet or continuous drought conditions, these parameters were reduced, reflecting the inhibitory effect of reduced water on selenium release and migration. Although the release rate of selenium under alternating dry-wet conditions was lower than that under continuous wet conditions, its activity was still higher than that under continuous drought conditions, which is because periodic water replenishment helps to maintain the solubility and diffusion capacity of selenium.

Previous studies have focused on the behavior of selenium under static conditions, emphasizing the important effects of drip irrigation and soil type on the migration and distribution of selenium, and pointing out the limitations of methods such as chemical extraction and isotope tracking in evaluating the bioavailability of selenium. In contrast, this study used DGT technology to capture the dynamic changes of selenium in complex environmental media in real time, providing more accurate quantitative data. At the same time, combined with adsorption isotherm determination and kinetic analysis, it deepened the understanding of the behavior of selenium at the soil-solution interface and clarified the applicability of the first-class kinetic model in describing the selenium release process.

Soil selenium content has a direct impact on crop nutrition, agricultural product quality and food safety, so accurately grasping the dynamic behavior of selenium is crucial to optimizing farmland management. This study provides a new perspective for understanding the behavior of soil selenium under long-term water regulation and verifies the effectiveness and reliability of DGT technology in this field. Through comparative analysis of selenium release rate, migration coefficient and bioavailability parameters under different water conditions, this study not only enriches the existing theoretical system but also lays the foundation for formulating scientific soil selenium resource management and ecological protection strategies. Future research should continue to explore how to translate these findings into practical guidelines to promote sustainable agricultural development and protect public health.

5. Conclusions

This paper uses thin-film diffusion gradient technology, combined with adsorption isotherms and kinetic models, to reveal the release and migration laws of soil selenium under long-term moisture changes. The experiment finds that the continuous wet conditions keep the selenium release rate relatively stable, eventually reaching 1.85 $\mu g \cdot cm^{-2} \cdot h^{-1}$, while the wet-dry alternating and continuous dry conditions drop to 1.42 $\mu g \cdot cm^{-2} \cdot h^{-1}$ and 0.88 $\mu g \cdot cm^{-2} \cdot h^{-1}$, respectively. The bioavailability index of selenium is the highest under wet conditions. Experimental data shows that moisture regulation significantly affects the migration coefficient of selenium in soil, which changes from 18.0×10^{-3} $cm^2 \cdot h^{-1}$ to 12.0×10^{-3} $cm^2 \cdot h^{-1}$ and 7.5×10^{-3} $cm^2 \cdot h^{-1}$ to 4.0×10^{-3} $cm^2 \cdot h^{-1}$ under wet and dry conditions, respectively. The high efficiency of DGT technology in monitoring and quantifying soil selenium behavior is verified through model fitting. The study provides a quantitative basis for the bioavailability of soil selenium under dynamic moisture conditions, providing theoretical support for optimizing selenium management, but it still needs to be expanded to other soil types and verification under seasonal moisture variation conditions. In the future, the research on the environmental behavior of soil trace elements can be deepened by improving the multi-element adaptability and monitoring accuracy of DGT technology.

Author Contributions

Conceptualization, Y.Z. (Yu Zhang 1), Y.L. Y.C and X.W.; methodology, Y.C.; software, Y.Z. (Yu Zhang 1); Y.Z. (Yu Zhang 2); validation, Y.C., X.W. and L.Z.; formal analysis, L.Z.; investigation, Y.Z. (Yu Zhang 1); resources, L.Z.; data curation, X.X.; writing—original draft preparation, Y.Z. (Yu Zhang 1); writing—review and editing, Y.Z. (Yu Zhang 2); visualization, Y.Z. (Yuxin Zhang); supervision, Y.Z. (Yu Zhang 2) and Y.Z. (Yuxin Zhang); project administration, Y.Z. (Yu Zhang 1); funding acquisition, Y.Z. (Yu Zhang 2). All authors have read and agreed to the published version of the manuscript.

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No new data were created.

Conflicts of Interest

The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript; or in the decision to publish the results.

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