

## Article

# A Polymer Inclusion Membrane for Sensing Metal Complexation in Natural Waters

Berta Alcalde, Enriqueta Anticó  and Clàudia Fontàs \* 

Chemistry Department, University of Girona, C/Maria Aurèlia Capmany, 69, 17003 Girona, Spain; berta.alcalde@udg.edu (B.A.); enriqueta.anticó@udg.edu (E.A.)

\* Correspondence: claudia.fontas@udg.edu

**Abstract:** Metal speciation studies are of great importance in assessing metal bioavailability in aquatic environments. Functionalized membranes are a simple tool to perform metal chemical speciation. In this study, we have prepared and tested a polymer inclusion membrane (PIM) made of the polymer cellulose triacetate (CTA), the extractant di-(2-ethylhexyl) phosphoric acid (D2EHPA), and the plasticizer 2-nitrophenyloctyl ether (NPOE) as a sensor for Zn and Cu complexation studies. This PIM, incorporated in a device with an 0.01 M HNO<sub>3</sub> receiving solution, is shown to effectively transport free metal ions, and it is demonstrated that the presence of ligands that form stable complexes with divalent metallic ions, such as ethylenediaminetetraacetic acid (EDTA) and humic acid (HA), greatly influences the accumulation of the metals in the receiving phase due to the increasing metal fraction complexed in the feed phase. Moreover, the effect of major ions found in natural waters has been investigated, and it is found that the presence of calcium did not decrease the accumulation of either Zn or Cu. Finally, the PIM sensor has been used successfully to evaluate metal complexation in a river water affected by Zn pollution.



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**Keywords:** polymer inclusion membrane; metal complexation; Zn; Cu; river water

## 1. Introduction

It is well known that metals in aquatic environments are found in numerous chemical or physical forms—such as free ions, inorganic and organic complexes, and colloidal forms. The dynamic process of metal partitioning depends on several chemical and physical parameters—such as the type and concentration of organic matter, ionic strength of the medium, hardness, pH, and redox conditions of the medium, among others. The combination of these abovementioned factors favors the formation of metallic species that can affect the metal bioavailability [1,2]. It is broadly accepted that the bioavailability and toxicity of metals cannot be predicted by total concentrations, but rather must be done by the concentration of various chemical species, in particular the free ions [3].

Electrochemical techniques—such as competing ligand equilibration-adsorptive cathodic stripping voltammetry (CLE-AdCSV), absence of gradient and Nernstian equilibrium stripping (AGNES), and stripping chronopotentiometry—can be useful for metal speciation studies [4]. Other techniques used in this field are the Donnan technique and permeation liquid membranes (PLMs), both based on semipermeable membranes. The Donnan technique consists of a membrane-based equilibrium process that exchanges ions between two solutions separated by an ion exchange membrane [5]. In contrast, the PLM technique is based on carrier-mediated transport of the metal of interest across a hydrophobic membrane from the sample solution into a strip solution, where it is accumulated [6,7]. The transport is based on liquid–liquid extraction coupled with diffusion. Under certain conditions, PLMs measure the free metal fraction but it has also been found that some lipophilic metal species cross the membrane and contribute to the total flux as a result of passive diffusion [4].

According to Buffle et al. [8], for the interpretation of PLM-based measurements in chemical speciation, it is useful to discriminate between different forms of the metal: the free form, the molecular sized complexes (where the ligand can be the proton inorganic anions or organic compounds), and colloidal or particulate species. Usually, colloidal or particulate species diffuse very slowly and cannot pass through the PLM. On the contrary, the free form of the metal, together with mobile species—including complexes and small colloidal species—contribute to a different extent to metal fluxes through the PLM and are relevant for bioaccumulation studies. In this respect, different research work has been reported in the literature for Zn, Ni, Cd, and Cu [6,9–11], being the lability of the metal complex, the lipophilicity, and the charge, key parameters affecting the PLM behavior.

Polymer inclusion membranes (PIMs) are another type of functionalized membranes where the carrier is entrapped within a polymeric matrix providing greater membrane stability than PLMs [12]. The most common polymers used to prepare PIMs are cellulose triacetate (CTA) or polyvinyl chloride (PVC). The selection of the carrier depends on the characteristics of the metal, and typical extractants used in solvent extraction are also suitable carriers for PIMs. Moreover, a plasticizer can be added to the membrane formulation both to improve membrane flexibility and to favor the diffusion of the complex formed by the metal and the carrier [13]. Various studies have used the carrier di-(2-ethylhexyl) phosphoric acid (D2EHPA) incorporated in PIMs for the transport of divalent metals, such as Zn and Cu. Szczepanski evaluated the simultaneous transport of Zn, Cd, Cu, and Pb through a PIM consisting of 38% CTA, 43% D2EHPA, and 19% of the plasticizer 2-nitrophenyloctyl ether (NPOE) using a 0.5 M HNO<sub>3</sub> solution as a receiving phase [14]. A PIM made of 60% PVC and 40% D2EHPA was also the basis of a new passive sampler developed to measure Zn ion in urban waters [15]. Kavitha et al. prepared a PIM that consisted of CTA, D2EHPA, and the plasticizer di-octyl phthalate (DOP) to selectively separate Cu(II) from the digested e-waste in the presence of heavy metal ions [16].

PIMs have recently shown their effectiveness as sensors for the determination of metal bioavailability in different media. Vera et al. developed a new tool for the determination of Zn free metal ion concentration using a PIM made of 70% PVC and 30% D2EHPA [17] in a hydroponic media in which potato plants (*Solanum tuberosum*) were also grown for purposes of comparison. It was found that the presence of different ligands—such as ethylenediaminetetraacetic acid (EDTA), humic acid (HA), and citrate—greatly influenced the measured Zn flux through the membrane due to the formation of metal complexes in the feed phase. Motsoane et al. developed a passive sampler for Cu, Ni, Co, and Cd in surface waters using a membrane made of 60% PVC and 40% D2EHPA using a 1.0 M HNO<sub>3</sub> solution as a receiving phase [18]. Similarly, a PIM made of 50% CTA, 20% NPOE, and 30% of the ionic liquid Cyphos 104 was investigated as a simple tool to monitor Zn in polluted river water [19]. The comparison of the metal measured by the PIM sensor and the metal accumulated by biofilm grown in the same water showed the suitability of the membrane to perform metal bioavailability studies.

In the present study, we investigate the use of a PIM containing the extractant D2EHPA as a tool for a rough estimation of the degree of divalent metal complexation in natural waters. The sensor developed is similar to that reported in [17], where the following assumptions were considered: fast kinetics for the interfacial reactions and fast diffusion of the metal in the sample solution under the selected stirring conditions. The accumulation of both Zn and Cu ions has been investigated using a nitric acid solution as a receiving phase, and the effect of ligands or possible interfering ions have been evaluated, among other parameters. Finally, the novel sensor has been used for the evaluation of Zn complexation in river water affected by abandoned mine drainage.

## 2. Materials and Methods

### 2.1. Reagents and Solutions

Stock solutions (1000 mg L<sup>-1</sup>) of Cu and Zn were obtained from Sigma-Aldrich (Saint Louis, MO, USA) and from SPEX CertiPrep (Metuchen, NJ, USA), respectively. KNO<sub>3</sub>

(99.0%), EDTA (disodium salt) (99.0–101.0%), and HNO<sub>3</sub> for analysis (65%) were from Panreac, Castellar del Vallès, Spain) and 2-(N-morpholino ethane sulfonic acid (MES, ≥99%) and HA sodium salt technical grade were purchased from Sigma-Aldrich (Saint Louis, MO, USA).

Solutions of 200 mg L<sup>-1</sup> HA, 10 mM EDTA, and 0.5 M MES were prepared using the above-mentioned reagents.

Feed solutions containing Zn or Cu in the range 0.001 to 0.03 mM (from the 1000 mg L<sup>-1</sup> stock solution) in 0.01 M KNO<sub>3</sub> and 0.01 M MES (to obtain pH = 6.0 ± 0.3) were prepared.

The evaluation of the effect of ligands was done by adding the corresponding amount of the stock solutions of EDTA or HA to a 0.03 mM metal solution in nitrate media at pH = 6.0 ± 0.3.

Simulated natural water (SNW) consisted of 2 mM NaHCO<sub>3</sub> pure pharma grade (99.0–100.5%), 0.5 mM Na<sub>2</sub>SO<sub>4</sub> Reag. Ph Eur (≥99.0%), both reagents purchased from Merck (Darmstadt, Germany), and 1 mM calcium CaCl<sub>2</sub> for analysis (98.0%), obtained from Panreac (Castellar del Vallès, Spain). In this solution, pH was also adjusted at 6.0 ± 0.3 using MES.

Competitive studies were done fixing the Zn content in 0.03 mM and varying Cu concentration from 0.008 to 0.03 mM in two different media: 0.01 M KNO<sub>3</sub> and SNW (both at pH 6).

In all cases, a 0.01 M HNO<sub>3</sub> solution was used as a receiving phase.

For the PIMs preparation, the polymer CTA was purchased from Across Organics (Geel, Belgium), the carrier D2EHPA (97%), the plasticizer NPOE (≥99.0%), and the organic solvent chloroform (CHCl<sub>3</sub>, ≥99.8%) were provided by Sigma-Aldrich (Saint Louis, MO, USA).

All reagents and solvents were of analytical grade and the ultrapure water used to prepare the aqueous solutions were obtained using the Milli-Q Plus water purification system (Millipore Ibérica S.A., Barcelona, Spain).

## 2.2. Instruments

Inductively coupled plasma optical emission spectrometry (ICP-OES, model 5110 from Agilent Technologies (Tokyo, Japan)) was used to determine total metal concentrations. The conductivity and the pH values were determined with an Ecosan, Entech Instruments, portable conductivity meter (Katey, TX, USA), and a Crison Model GLP 22 pH meter (Barcelona, Spain), respectively.

Major ions were measured using ion chromatography (IC) IC55000 from DIONEX (Sunnyvale, CA, USA) equipped with an autosampler AS-AP and a conductivity detector. The columns used were an IonPac<sup>®</sup> AS18 anion-exchange column (4 × 250 mm) with the AG Guard column (4 × 40 mm) for anions and a IonPac<sup>®</sup> CS16 cation-exchange column (4 × 250 mm) with the CG16 Guard column (4 × 50 mm) for cations. Alkalinity was determined using Metrohm Titrosampler 855 (Herisau, Switzerland). Total organic carbon (TOC) was determined using a TOC-V CSH (230 V) from Shimadzu (Kyoto, Japan).

## 2.3. PIMs Preparation

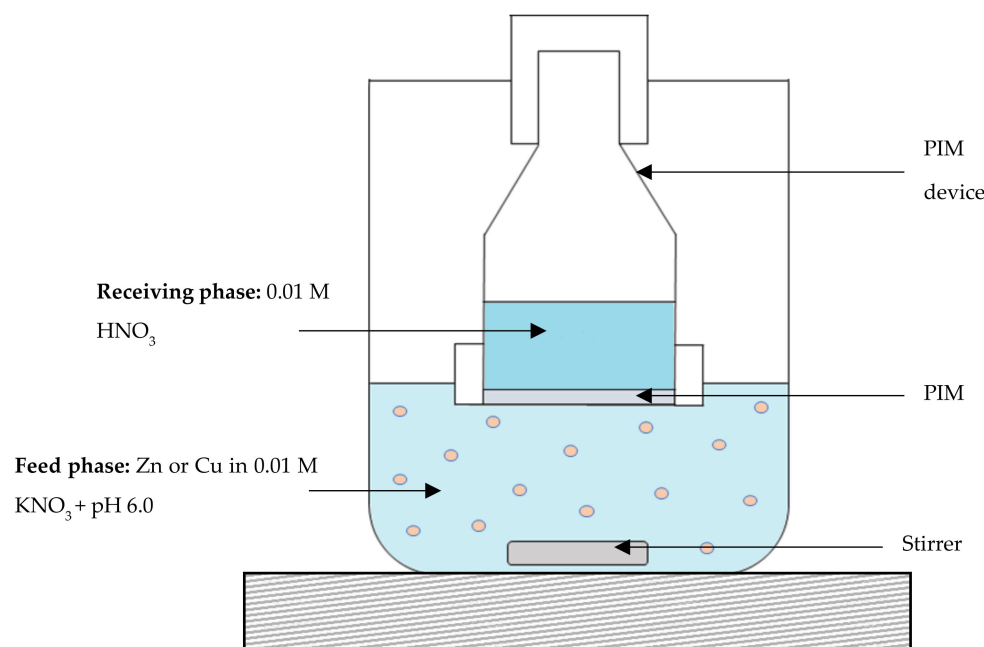
PIMs were prepared using the solvent casting method [20]. In summary, a specific amount of CTA (0.20 g) was dissolved in 20 mL of CHCl<sub>3</sub> and maintained under stirring for 5 h. The carrier (D2EHPA) and the plasticizer (NPOE) were then added, and the resulting mixture was stirred for one hour more. Afterwards, the solution was poured into a 9.0 cm diameter flat bottom glass Petri dish, which was set horizontally and covered loosely for 24 h. The membrane was then carefully peeled off the bottom of the Petri dish to obtain the PIM. Circular pieces with an area of 1.77 cm<sup>2</sup> were cut from the membrane central section and used in the experiments. The composition of the prepared membranes is listed in Table 1.

**Table 1.** Composition of the PIMs studied in this work expressed in % mass. The amount of each component (g) is indicated in parentheses.

Membrane	Polymer (CTA)	Carrier (D2EHPA)	Plasticizer (NPOE)
M1	50% (0.20)	50% (0.20)	-
M2	50% (0.20)	40% (0.16)	10% (0.04)
M3	50% (0.20)	30% (0.12)	20% (0.08)

#### 2.4. Experimental Procedure

The design of the device used was similar to those previously reported by Almeida et al. and Vera et al. [17,21]. It consisted of a glass vessel with two openings with a screw thread on each. The bottom opening (1.8 cm diameter) was used to expose the membrane to the feed solution; the membrane was fixed using a rubber ring and a screw cap. The top opening (0.9 cm diameter) was used to fill the device with the receiving solution (5 mL of 0.01 M HNO<sub>3</sub>) and it was also closed with a screw cap. The PIM device was contacted with 100 mL of feed solution (1 cm immersed) which was continuously stirred (see Figure 1) and at the end of the experiment, both receiving and feed solutions were taken for analysis.



**Figure 1.** Scheme of the experimental setup.

Using this setup, different studies were performed using the appropriate feed solutions for the effect of metal concentration, competitive studies, and the effect of ligands. Moreover, a river water sample was also analyzed and used as received (no filtration or pH adjustment).

All experiments were at least performed in triplicate and the temperature was kept within the range of  $22 \pm 1$  °C.

For Zn/Cu competitive studies, the accumulation efficiency was calculated by means of Equation (1)

$$\text{Accumulation efficiency (\%)} = \frac{V_r}{V_f} \cdot \frac{[M]_{r,t}}{[M]_{f,0}} \times 100 \quad (1)$$

where  $V_r$  denotes the volume of the receiving solution,  $V_f$  the volume of the feed solution,  $[M]_{r,t}$  the metal concentration of the receiving solution at a certain time, and  $[M]_{f,0}$  the metal concentration of the initial feed solution.

To evaluate the results of the real water sample, the metal accumulated in the receiving solution was correlated with the free metal concentration by means of an experimental calibration curve.

### 2.5. Data Analysis

The speciation calculations of this study have been carried out using Visual MINTEQ software (Stockholm, Sweden). Statistical tests have been performed using the Excel package (Microsoft, Redmond, Washington, DC, USA).

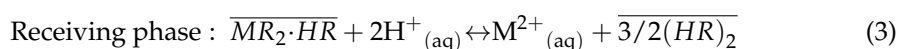
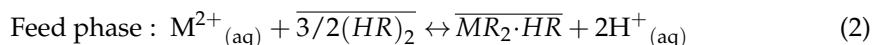
### 2.6. Sampling Site and Natural Water Experiments

The Osor River (41°57'14" N, 2°35'58" E), located in North-East Catalonia (Spain), is a small tributary of the Ter River. It was selected for this study because of its high Zn content due to past mining activity that has affected the river water composition [19]. The water sample was taken in a 1 L clean plastic bottle and transported under refrigeration to the laboratory.

## 3. Results

### 3.1. Evaluation of PIM Composition

Divalent metals such as Zn and Cu can be accumulated in the receiving solution through the PIM. The incorporation of D2EHPA in the membrane allows the extraction and back-extraction of metal ions simultaneously. As reported in several studies [22,23] the mechanism of the divalent ion complexation with the carrier D2EHPA can be described by the following stoichiometric equations (Equations (2) and (3)).

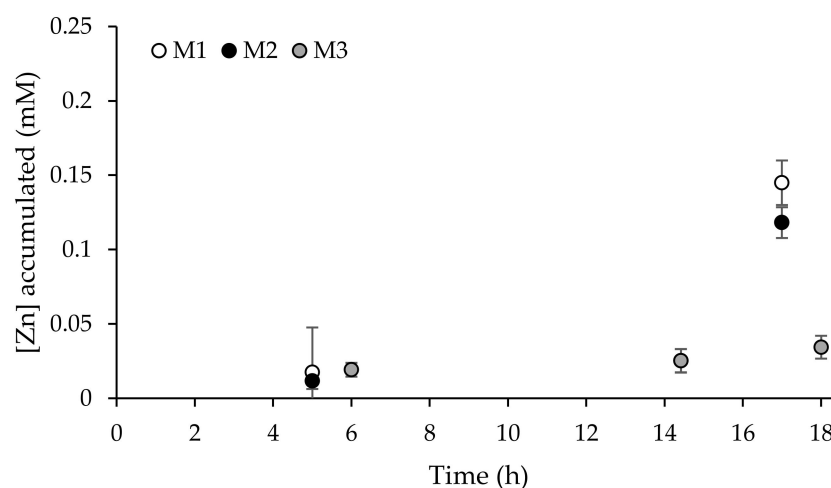


where *HR* denotes the carrier (D2EHPA) molecule and  $M^{2+}$  the divalent cations,  $Zn^{2+}$  or  $Cu^{2+}$ .

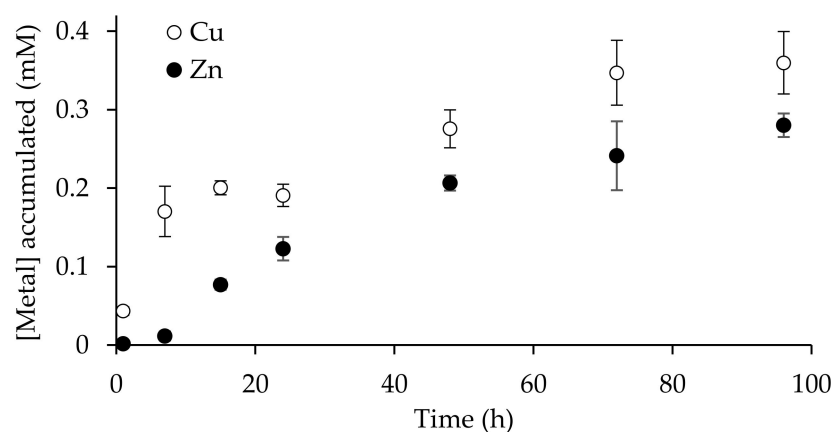
Even though the carrier has the central role in the transport process through the membrane, it is well known that the other components of the PIM composition are also of great importance for the transport of the metals [24]. Therefore, different PIMs were prepared (Table 1) and their effectiveness was investigated in terms of Zn accumulation at different times. The results are presented in Figure 2. As can be seen, for M1 (PIM without any plasticizer) the accumulated Zn in the receiving phase increased with time. However, this membrane was highly brittle and difficult to manipulate. In order to improve the mechanical characteristics of the membrane, the addition of the plasticizer NPOE to the formulation of the PIM was investigated (M2 and M3). It was found that M2 had similar behavior to M1, but that the addition of plasticizer improved its mechanical stability. In the case of M3, the metal accumulation was less efficient. According to Nghiem et al., this could be due to an excess of plasticizer causing an additional barrier to zinc transport by forming a film on the membrane surface [25]. Consequently, further experiments were performed using M2.

### 3.2. Accumulation of Zn and Cu: Individual Studies

The accumulation of both Zn and Cu was investigated using the PIM device at different times. As can be seen in Figure 3, even though both metals were effectively transported, the accumulation of Cu was faster than Zn at the initial times. Moreover, the system seems to approach equilibrium at  $t > 100$  h bringing about a considerable depletion of the feed solution (46% for Zn and 60% for Cu). As this specific study is aimed at providing data on the possibility of using the PIM system as a tool for the rough estimation of the two main metal fractions in the water sample, avoiding long depletion times and using reasonable volumes of the feed solution (to be measured in the laboratory), we chose 24 h as the experimental time for further experiments.



**Figure 2.** Effect of PIM composition on Zn accumulation at different times. Feed phase: 100 mL of a 0.03 mM Zn in 0.01 M  $\text{KNO}_3$ , pH 6.0; PIMs: M1–M3; receiving phase: 5 mL 0.01 M  $\text{HNO}_3$  ( $n = 3$ ).



**Figure 3.** Metal accumulation at different times (individual studies). Feed phase: 100 mL of a 0.03 mM Zn or Cu in 0.01 M  $\text{KNO}_3$ , pH 6.0; PIM: M2; receiving phase: 5 mL 0.01 M  $\text{HNO}_3$  ( $n = 3$ ).

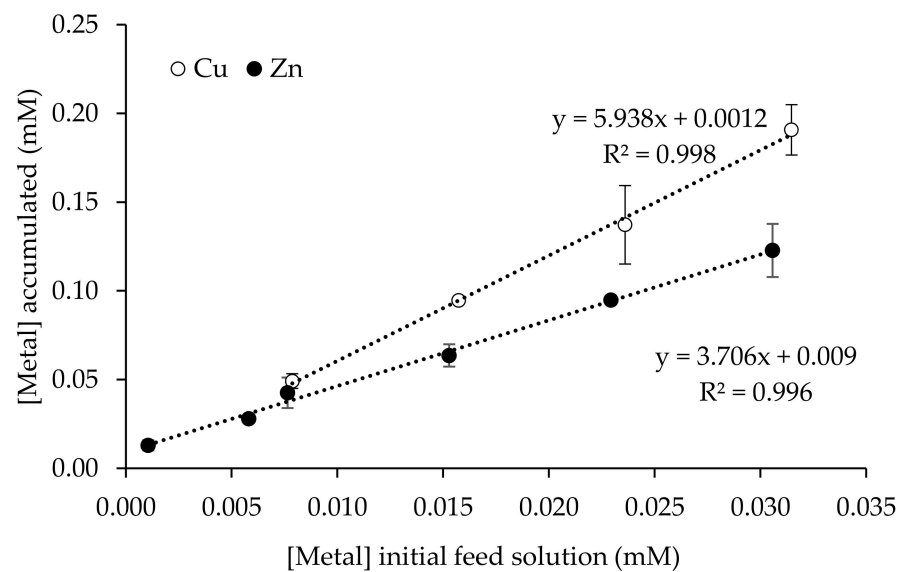
For both Zn and Cu, the effect of the initial metal concentration (in the range 0.001–0.03 mM for Zn and 0.008–0.03 mM for Cu) on their accumulation in the receiving phase was studied. The results are presented in Figure 4, where it can be seen that the relationship between the metal accumulated in the receiving phase and the metal initially present in the feed phase follows a linear trend, with the accumulation of Cu being higher than Zn, under the same conditions.

Taking into account that—according to MINTEQ calculations—Zn and Cu are present as free ions at the studied pH and  $\text{KNO}_3$  medium, the obtained relationship can be used as a calibration curve for the estimation of free metal ions by measuring the metal accumulated in the receiving solution.

### 3.3. Effect of the Metal Complexation

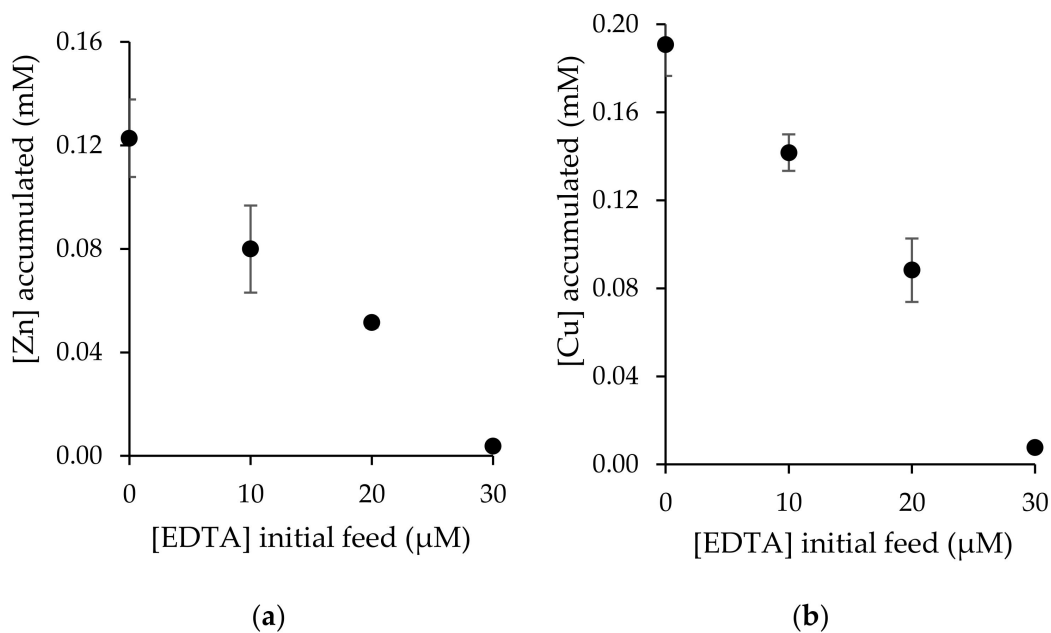
To test the feasibility of the developed PIM as a tool to evaluate metal complexation, two organic ligands have been used: EDTA, forming stable complexes with divalent metal ions, and humic acids, which are present in natural waters.

For that, we previously checked using Visual MINTEQ software and an appropriate range of EDTA to obtain solutions with different free metal content when fixing the total metal concentration at 0.03 mM. Therefore, the evaluated EDTA range was 0–30  $\mu\text{M}$ . In the case of Zn, free metal was 98% when no EDTA was added, 66% at 10  $\mu\text{M}$  EDTA, 34% at 20  $\mu\text{M}$  EDTA, and 2% at 30  $\mu\text{M}$  EDTA. In the case of Cu, the free metal was 97%, 66%, 35%, and 5%, respectively.



**Figure 4.** Effect of the initial metal concentration in the feed phase (individual studies) on metal accumulation. Feed phase: 100 mL of a 0.001 to 0.03 mM for Zn and 0.008 to 0.03 mM for Cu in 0.01 M  $\text{KNO}_3$ , pH 6.0; PIM: M2; receiving phase: 5 mL 0.01 M  $\text{HNO}_3$  ( $n = 3$ ).

Figure 5 shows the results of the accumulated metal using the PIM sensor vs. EDTA concentration in the feed solution, (a) for Zn and (b) for Cu. As can be observed, in both cases, the metal accumulated in the receiving phase diminished when the amount of EDTA increased, being almost zero at 30  $\mu\text{M}$  EDTA (where only 2% of Zn and 5% of Cu are present as a free species according to the MINTEQ calculations). These findings support the fact that the PIM is able to distinguish between strongly complexed metal species and free metal ions. Moreover, the variation of metal accumulated seemed to correlate well with the content of both free Zn or Cu initially present in the feed solution, estimated with the calibration curves shown in Figure 4.



**Figure 5.** Effect of EDTA on metal accumulation. Feed phase: 100 mL of 0.03 mM of Zn (a) or Cu (b) in 0.01 M  $\text{KNO}_3$ , pH 6.0 and EDTA: 0 to 30  $\mu\text{M}$ ; PIM: M2; receiving phase: 5 mL 0.01 M  $\text{HNO}_3$  ( $n = 3$ ).

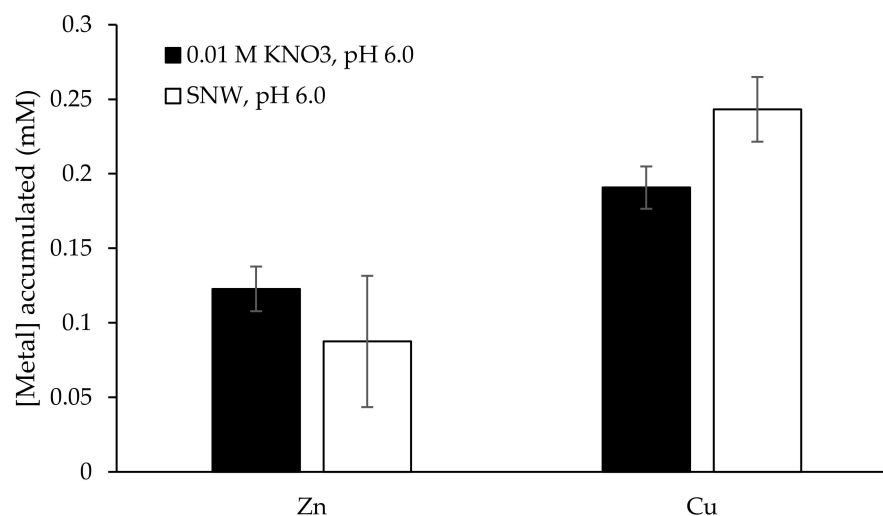
HA were also tested as a ligand for both Zn and Cu, using as a feed solution a 60 mg L<sup>-1</sup> HA in 0.01 M KNO<sub>3</sub> at pH 6 with a total metal concentration of 0.03 mM. It was found that, under these conditions, the metal accumulated in the receiving phase was 0.09 mM for Zn and 0.02 mM for Cu. The fact that, in the absence of HA, the metal accumulated was higher (0.12 mM for Zn and 0.19 mM for Cu) gives more evidence that the PIM sensor is sensitive at the presence of ligands that either diminish the free metal content or form complexes that cannot pass through the PIM.

Consequently, these results show the feasibility of the developed PIM sensor to measure metal complexation in a controlled medium.

### 3.4. Competitive Studies

The ability of D2EHPA to accumulate metal cations in a similar manner (non-selective carrier) was further investigated in (i) SNW solution, where Ca<sup>2+</sup> and other ions are present; and (ii) mixtures of Cu and Zn.

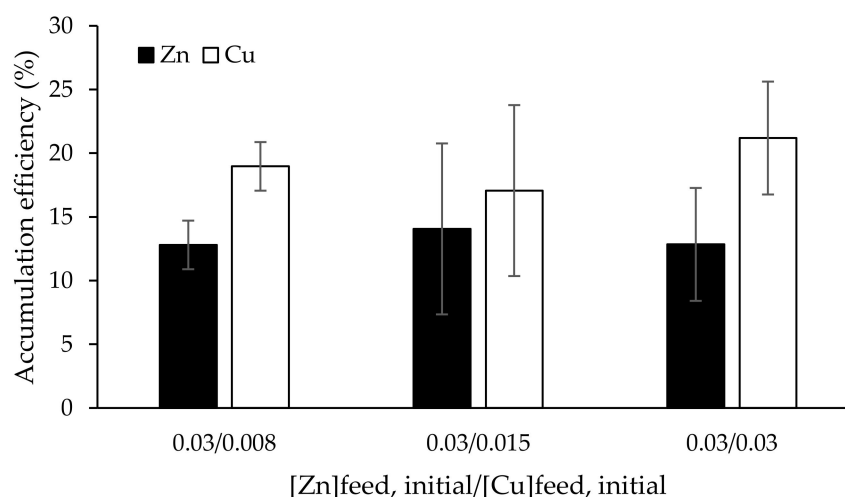
In the first case, experiments were conducted to determine whether or not the presence of calcium could affect the accumulation of either Zn or Cu. Calcium is a divalent cation that is widely present in natural waters and that can also be extracted by D2EHPA [26]. These experiments were performed using as a feed solution a SNW containing 1 mM Ca<sup>2+</sup>, among other ions (see Section 2.1), and only 0.03 mM of Zn or Cu. The results are presented in Figure 6 for each metal, where the accumulation obtained in controlled medium (nitrate at pH = 6) is compared to that in SNW. In the case of Zn, the accumulated metal was not statistically different at the 95% confidence (*t*-test), while in the case of Cu, its accumulation in SNW increased slightly. Therefore, even though the high amount of Ca present in water, besides other ions, the effectivity of the PIM system to accumulate both Zn and Cu was not affected as has already been discussed in Fontàs et al. [27].



**Figure 6.** Effect of the matrix on metal accumulation. Feed phase: 100 mL of a 0.03 mM of Zn or Cu in 0.01 M KNO<sub>3</sub>, pH 6.0 or in SNW, pH 6.0; PIM: M2; receiving phase: 5 mL 0.01 M HNO<sub>3</sub> (*n* = 3).

Moreover, competitive experiments were conducted with Zn/Cu mixtures in 0.01 M KNO<sub>3</sub> at pH 6. In these experiments, the Zn concentration was set at 0.03 mM and the Cu concentration was varied from 0.008 to 0.03 mM. In this case, the results of which are presented in Figure 7, the accumulation efficiency was calculated for each metal found in the receiving solution. As can be seen, the accumulation of Zn was not affected even though Cu was also effectively transported through the PIM in the evaluated concentration range.





**Figure 7.** Effect of Cu presence on Zn accumulation. Feed phase: 100 mL of a 0.03 mM Zn and 0.008 to 0.03 mM of Cu in 0.01 M  $\text{KNO}_3$ , pH 6.0; PIM: M2; receiving phase: 5 mL 0.01 M  $\text{HNO}_3$  ( $n = 3$ ).

These results show the PIM system to be a suitable tool for environmental studies to evaluate the free/complexed fraction of metal in natural waters.

### 3.5. Evaluation of Zn Speciation in a River Water Sample

The developed PIM sensor was used to determine Zn complexation of a water collected in Osor River. As mentioned in the experimental section, this river receives inputs from an abandoned mine, resulting in an abnormal Zn concentration in the water. This water also contains trace levels of Fe, Cu, and Mn [28].

The water sample was fully characterized, and the results are shown in Table 2. No Cu was detected at levels higher than the LOD of the instrument ( $20 \mu\text{g L}^{-1}$ ). Moreover, at this particular sampling point, water had high conductivity, which is attributed mainly to sulphate ions originating from the mineral content of the soil.

**Table 2.** Water physico-chemical parameters at the sampling point of the Osor River.

Parameters	Value	Parameters	Value
pH	7.67	Alkalinity	$144.90 \text{ mg HCO}_3^- \text{ L}^{-1}$
Conductivity	$601 \text{ mS cm}^{-1}$	$[\text{NO}_3^-]$	$1.04 \text{ mg L}^{-1}$
$[\text{Zn}^{2+}]$	$0.76 \text{ mg L}^{-1}$ ( $=0.012 \text{ mM}$ )	$[\text{PO}_4^{3-}]$	$0.12 \text{ mg L}^{-1}$
$[\text{Cu}^{2+}]$	n.d.	$[\text{Cl}^-]$	$16.24 \text{ mg L}^{-1}$
$[\text{Na}^+]$	$31.26 \text{ mg L}^{-1}$	$[\text{SO}_4^{2-}]$	$132.89 \text{ mg L}^{-1}$
$[\text{K}^+]$	$3.77 \text{ mg L}^{-1}$	$[\text{F}^-]$	$1.66 \text{ mg L}^{-1}$
$[\text{Ca}^{2+}]$	$130.38 \text{ mg L}^{-1}$	TOC	$0.92 \text{ mg C L}^{-1}$
$[\text{Mg}^{2+}]$	$15.23 \text{ mg L}^{-1}$		

n.d.—not detected.

This water sample was analyzed using the PIM sensor. It is important to point out that water samples did not receive any treatment before their analysis. The metal measurement of the receiving solution revealed an accumulation of  $0.034 \pm 0.001 \text{ mM}$  Zn. This value represents a 78% decrease of the accumulation value ( $0.15 \text{ mM}$ ) calculated using the calibration curve shown in Figure 4 (which considers all metal as a free species). Taking into account that the extraction of both Zn and Cu with D2EHPA is not affected at  $\text{pH} > 5$  [15,29,30] results obtained with the PIM device can be related with the complexation of metal in the water sample.

This result may be relevant from the point of view of the impact of the metal on the ecosystem.

#### 4. Conclusions

In this study, we have developed a simple sensor based on a polymer inclusion membrane consisting of 50% CTA, 40% D2EHPA, and 10% NPOE to evaluate metal complexation in natural waters. When this PIM is incorporated in a device containing an 0.01 M HNO<sub>3</sub> solution as the receiving phase, the metals studied (Zn and Cu) can be accumulated to different extents, varying in accordance with the presence of metal ligands. Therefore, it has been proven that the presence of EDTA and humic acids reduces the accumulation of Zn and Cu. It was found that neither Ca or the simultaneous presence of Zn and Cu affects the percentage of metal accumulated in the receiving solution. The feasibility of applying the PIM device developed to polluted river waters was demonstrated by measuring complexed Zn in an Osor River water sample.

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**Conflicts of Interest:** The authors declare no conflict of interest.

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