ADSORPTION OF METALS TO MEMBRANE FILTERS IN VIEW OF THEIR SPECIATION IN NUTRIENT SOLUTION

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Abstract—Filtration of a solution may lower metal concentrations through adsorption of metal species to the filter. Processes such as filter-sterilizing nutrient solution and filtration of field water are sensitive to these sorption artifacts, yet basic data on the affinity of different filters for metals are lacking. This article describes the adsorption of five metals to eight types of 0.2-μm membrane filters used for sterilizing a plant (Lemna minor L.) culture medium. Filters of cellulose acetate, cellulose nitrate, mixed cellulose ester, nylon, polyamide, polycarbonate, polyester, and polyvinylidene fluoride were tested for their affinity toward mono- (K), di- (Mn, Cu, Zn), and trivalent (lanthanum [La]) metals. Metal concentrations were quantified using radioisotopes and speciation was calculated. Results showed that metals had the lowest affinity for polycarbonate and nylon filters and the highest affinity for cellulose- and polyester-type filters. Furthermore, it was shown that the metal load on cellulose filters correlated best with free ion concentrations (indicating electrostatic attraction), while loads on other filters correlated better with total metal concentrations. Filtering a 5-ml solution of pH 5 did not affect its metal concentrations, ranging from 10 nM (La) to 49 μM (K). To minimize filtration artifacts, we propose using polycarbonate or nylon filters, especially when dealing with low volumes of high pH and low metal species concentrations.

Keywords—Sterile filtration Culture medium Lemna minor Radioisotope Lanthanum

INTRODUCTION

Sterilization of aqueous solutions, such as nutrient media used for culturing and testing algae and higher plants, is done by filtration through a pore size of 0.2 μm [1,2], autoclaving at 121°C, or by combining the two [3]. These techniques are applied in order to avoid undesired influences of bacteria, fungi, or (other) algae in otherwise controlled experiments. The idea is to kill the microorganisms by autoclaving or separate them from solution by filtration while not affecting the chemical composition of the medium itself. Both methods have drawbacks and the decision to use either of them should be based on the specific further use and characteristics of the sterilized solution. Microorganisms are killed in autoclaved solutions, while filter sterilization removes them from solution. Autoclaving increases the solution’s temperature to 121°C, so it must be cooled before use; filtered solutions are ready for immediate use. Sterile filtration of small volumes through a syringe filter requires a large differential pressure and yields less filtrate than autoclaving because some solution is lost in the void volume of the filter and filter holder [4,5]. Another disadvantage of filtration is that sterile filters are relatively expensive and nonsterile filters require sterilization before they can be used. A disadvantage of autoclaving is that the high temperature can cause irreversible chemical reactions to occur. Examples are the escape of CO2 (g) from the solution’s carbonate system and the damaging effect of autoclaving on ethylenediaminetetraacetic acid (EDTA) [6].

Possible damage to organic chemicals could be the decisive factor for choosing filtering instead of autoclaving a solution [2]. Few organic substances are present in nutrient solutions, e.g., a metal chelator (such as EDTA) and optionally a pH buffer (such as 2-morpholinoethane sulfonic acid [MES]); the main part of the medium is made up of inorganic components. It is unlikely that inorganic medium components except the above-mentioned carbonate suffer from autoclaving, but it has been shown that membrane filters have some affinity for cations and metal complexes [7–10]. The speciation and charge of a metal are consequently of great importance. Some data concerning the influence of filtration on metal concentrations in solution are available, but they do not reveal if metals are adsorbed to the filter or are retained because they are present in or sorbed to particles exceeding the pore size [8,11,12]. Consequently, there is a need for basic data evaluating the compatibility of different filter types with various metals in solution [7,8,13]. Such data may also be of use in studies on natural waters, where filtration is used to separate dissolved metals from particulates.

The purpose of this work was to evaluate the suitability of eight filter types for the sterilization of nutrient solutions with respect to the adsorption of mono-, di-, and trivalent metal cations or complexes. Chemical speciation of the metals was calculated to assess its importance for adsorption, while the use of radioisotopes permitted sensitive measurements of metal concentrations in both filters and filtrates. The results and their validity for other metal-containing solutions, e.g., natural waters, are discussed in view of the speciation of metals in solution.

MATERIALS AND METHODS

Nutrient solution

The nutrient solution evaluated in this assessment was adapted from the Swedish Standards Institute [14] and was...
Table 1. Composition of *Lemna minor* nutrient medium, adapted from the Swedish Standards Institute [14], concentrations in mol/L (M)

<table>
<thead>
<tr>
<th>Component</th>
<th>Concentration (M)</th>
<th>Component</th>
<th>Concentration (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaNO₃</td>
<td>5.00 × 10⁻⁴</td>
<td>CuSO₄·5H₂O</td>
<td>2.00 × 10⁻⁸</td>
</tr>
<tr>
<td>KH₂PO₄</td>
<td>4.92 × 10⁻³</td>
<td>Co(NO₃)₂·6H₂O</td>
<td>3.44 × 10⁻⁸</td>
</tr>
<tr>
<td>MgSO₄·7H₂O</td>
<td>3.04 × 10⁻³</td>
<td>NaVO₃</td>
<td>8.20 × 10⁻⁸</td>
</tr>
<tr>
<td>CaCl₂·2H₂O</td>
<td>2.45 × 10⁻⁴</td>
<td>FeCl₂·6H₂O</td>
<td>3.11 × 10⁻⁸</td>
</tr>
<tr>
<td>H₂BO₃</td>
<td>1.62 × 10⁻⁶</td>
<td>Na₂EDTA·2H₂O</td>
<td>5.37 × 10⁻⁶</td>
</tr>
<tr>
<td>MnCl₂·4H₂O</td>
<td>1.01 × 10⁻⁶</td>
<td>MES·H₂O</td>
<td>2.34 × 10⁻³</td>
</tr>
<tr>
<td>ZnSO₄·7H₂O</td>
<td>1.74 × 10⁻⁷</td>
<td>LaCl₃·7H₂O</td>
<td>1.00 × 10⁻⁸</td>
</tr>
<tr>
<td>Na₂MoO₄·2H₂O</td>
<td>4.13 × 10⁻⁸</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* The metal of this component was spiked with radioisotopes.
* EDTA = ethylenediaminetetraacetic acid.
* MES = 2-morpholinoethane sulfonic acid.

designed for the sterile culturing and testing of common duckweed (*Lemna minor* L.). This medium has minimal concentrations of nutrients compared with other culture media (e.g., Gorham’s medium [15], and for an overview of media, see Landolt and Kandelzer [16]) but resembles those observed in natural environments of *L. minor*. Its composition is given in Table 1. Adaptations made to the original medium include replacement of pH buffer 3-morpholinopropane sulfonic acid by MES for lower pH, omission of Na₂CO₃ because the main carbon source for *L. minor* is CO₂ from air [16], addition of NaVO₃ to supply plants with the essential element vanadium, and addition of a small amount of lanthanum (La), making up a final La concentration of 10 nM.

Lanthanum is normally not present in a nutrient solution (other than as a chemical impurity) but was added to incorporate a trivalent metal in the experiments and be able to study its sorption behavior next to that of mono- and divalent metals. Iron (Fe), the only trivalent metal present in the original medium, is less suitable with respect to the required radiochemical sensitivity (see Discussion section). In addition to La, we chose copper (Cu), zinc (Zn), potassium (K), and manganese (Mn) for this work because, at irradiation, they produce suitable γ-emitting isotopes, regarding both half-lives and characteristic photo peaks (Table 2).

**Production of radioisotopes**

Concentrated stock solutions of the metal salts, all reagent-grade chemicals, were prepared in Milli-Q® water (Millipore-Waters, Milford, MA, USA). From these solutions, three samples were prepared in quartz vials and irradiated for 24 h at a neutron flux of 1.60 × 10¹⁷/(m²·s) in the Hoger Onderwijs Reactor of the Interfaculty Reactor Institute in Delft, The Netherlands. The samples contained 2.0 × 10⁻⁴ mole CuSO₄·5H₂O plus 1.74 × 10⁻⁷ mole ZnSO₄·7H₂O in 500 μL to yield the radioisotopes ⁶⁵Cu, ⁶⁵Zn, and ⁶⁵⁶Zn (a metastable ⁶⁵⁶Zn isotope), 4.92 × 10⁻⁶ mole KH₃PO₄ in 500 μL to yield ⁴⁶K, and 1.0 × 10⁻⁸ mole LaCl₃·7H₂O in 100 μL to yield ¹⁴⁰La, respectively. The radioisotope ⁶⁸Mn was prepared by irradiating a polyethylene capsule containing 1.01 × 10⁻⁶ mole MnCl₂·4H₂O in 500 μL for 1 h at a neutron flux of 4.40 × 10¹⁵/(m²·s). Samples were cooled down for 3 h to eliminate short-lived radioisotopes such as ⁸⁶Cl, which has a half-life of 37.2 min. Specific activities of the isotopes at the starting time of the experiment are given in the Results.

**Handling of nutrient solution and filters**

The irradiated solutions were added to a volumetric flask already containing the nonradioactive solution components in approximately 500 ml Milli-Q water, and the volume was adjusted to 1 L. The pH was adjusted to 5.00 ± 0.01 with 0.2 N HNO₃ and 0.1 N NaOH. This results in a small net addition of nitrate or sodium, but due to the relatively high concentrations of these ions in the original nutrient solution (5.0 × 10⁻⁴ M and 5.1 × 10⁻⁴ M, respectively) and their weak interactions with other components, influence on medium speciation was insignificant (as shown by speciation calculations; see below). Finally, the nutrient solution was mixed thoroughly by gently shaking the flask.

The experiment included eight types of hydrophilic membrane filters: cellulose acetate (CA; Sartorius, Nieuwegein, The Netherlands), cellulose nitrate (CN), nylon (NY), and polyester (PE; Fisher Scientific, ‘s-Hertogenbosch, The Netherlands); mixed cellulose ester (MCE), polycarbonate (PC), and polyvinylidene fluoride (PVF; Millipore, Etten-Leur, The Netherlands), and polyamide (PA; Schleicher & Schuell, ‘s-Hertogenbosch, The Netherlands) with pore size 0.2 or 0.22 μm and a diameter of 25 mm. Polyamide filters were punched out of 50-mm-diameter filters. All filter types were readily available from laboratory suppliers and needed no pretreatment before filtration. Filters were handled with tweezers and placed in a filter holder of either polysulfone or PC. The filter holder with the membrane was screwed tightly on a syringe and exactly 5 ml medium was pipetted into the back of the syringe. The medium was pushed through the membrane and the final 2 ml were collected in preweighed tubes. Then the membrane was removed from the filter holder and put into a tube that was preweighed with a dry membrane. Also, 2 ml of unfiltered medium was pipetted in duplicate in preweighed tubes. All tubes and samples were weighed on an analytical balance (Mettler-Toledo, Greifensee, Switzerland) with an accuracy (standard deviation) of 0.00002 g to be able to correct for attached medium on the filters and differences in sample weight.

**Activity measurements**

Samples were measured with a well-type detector of high-purity germanium with a full width-half maximum of 2.4 keV at 1.332 keV (⁶⁰Co). Filling height corrections were made to account for differences in geometry of the samples. For interpreting gamma-ray spectra, ²⁴Na was taken into account, next to the six intentionally produced radionuclides, because ²⁴Na is nearly always produced during irradiations as a result of the omnipresent Na. Gamma-ray spectra were interpreted according to Blauw [17].

The samples were measured twice, immediately after the experiment (counting time 15 min per sample) and again after
6 d (counting time 4 h per sample) to optimize results for the long-lived isotopes $^{140}$La and $^{65}$Zn (see half-lives in Table 2). The two measurements were combined to produce final activities of radionuclides in the samples, calculated back to the starting time of the experiment. If the activity of a radioisotope was equal to or below the detection limit, it was estimated to be 20% of the detection limit (corresponding to a detection probability of 50%), with a standard deviation of twice that value [18]. Finally, activities (Bq) were converted to moles. To be able to calculate propagated errors in the metal amounts, an arbitrary error of 1% in stock solution concentrations was assumed.

Statistics and data handling

Data were reported as weighted means with standard errors of the mean (SEM, $n = 2$). Standard errors were calculated using common error propagation rules. A one-way analysis of variance (ANOVA) was applied to test differences between filters and between filtrates and unfiltered medium. This implies that values were assumed to come from a Gaussian population. This assumption seems justified because there are many independent error sources involved. A significant ANOVA ($p < 0.05$) was followed by a Tukey test to compare all pairs of means. Pearson’s correlation coefficients were calculated for metal amounts and charges on filters against total metal and free metal ion concentrations in solution. Finally, linear regression of logarithmically transformed metal amounts on filters against logarithmically transformed metal concentrations in solution was performed. The software program Prism, Ver 2.01 (GraphPad Software, San Diego, CA, USA), was used for all calculations.

Speciation calculations

To be able to assign chemical forms to each of the metals in the medium, equilibrium speciation calculations were performed with the software program CHEAQS (http://home.tiscali.nl/~vdieest11) [19]. Information from these calculations, i.e., the speciation of a metal in solution, may help explain its sorption behavior. Some changes and additions to the program’s stability constants database were made. Six constants for MES were added [20,21] and 12 constants for La were added or replaced [22–26]. Precipitation equilibria were included in the calculations and CO$_2$ (g) saturation of the solution was assumed, using the ambient partial pressure of this gas, $p_{CO_2} = 3.5 \times 10^{-4}$ atm [27]. This assumption seems reasonable because stock solutions and the final nutrient solution were open to exchange with the air above at all times. The CO$_2$ diffusion-derived carbonate in solution (total concentration 12.6 $\mu$M) is predominantly associated with H$^+$ (95.25% H$_2$CO$_3$ and 4.73% HCO$_3^-$) and only for about 0.01 and 0.02% with Mg$^{2+}$ and Ca$^{2+}$, respectively. Furthermore, calculations for a closed system showed that no significant change occurred in ionic strength or in the speciation of any of the metals studied. Redox equilibria, which are important for Mn speciation, among others, were not included in the calculations because Mn oxidation takes place at a rate too slow to be relevant within the timeframe of our experiments [27].

RESULTS

Measurements

The activity measurements of filters and filtrates, obtained with a filter holder of either polysulfone or PC, showed excellent agreement, and no losses of activity occurred. Hence, the filter holder material had no detectable influence on metal sorption to the filters. Therefore, observations obtained with different filter holders were treated as replicates. Specific activities were calculated from measurements of unfiltered medium at the starting time of the experiment and are given in Table 2. Combining specific activities with metal concentrations (Table 1) yields the activity concentrations, which are also given in Table 2. Zinc-65 had the lowest activity concentration (1.36 Bq/ml) and $^{62}$K the highest (1,730 Bq/ml). Because of the low $^{65}$Zn activity concentration and associated analytical difficulties, Zn data are calculated and presented primarily on the basis of the $^{62}$Zn measurements.

Metal concentrations in filtrates and unfiltered medium are given in Figure 1. The length of the error bars indicates that measurements of Cu and Zn were less reproducible than those of La, K, and Mn, which is related to the activity concentrations (Table 2). Significant differences were detected only for Mn between three filtrate types and the unfiltered medium. This
is probably due to the somewhat higher value for unfiltered medium and could not be explained by significant adsorption of Mn to the three filter types concerned. Moreover, Figure 1 shows that no significant losses occurred during filtration for any of the metals.

Results from the filter measurements are presented in Figure 2. Activities on filters were corrected for attached medium by calculating the attached volume from the weight measurements (varying roughly from 8 μl for PC to 80 μl for MCE) and subtracting the corresponding unfiltered medium activity of that volume. In three cases (once each for Mn, Zn, and Cu), correction procedures resulted in negative values for metal amounts, reflecting uncertainties in weighing but more importantly in activity measurements. This results from some activity measurements being equal to or below the detection limit (see section Activity measurements in Materials and Methods), while weights were established easily. However, negative values were not significantly different from zero (see Fig. 2). Although measurements of the filtrates showed no decrease in metal concentrations, adsorption of La, K, and Mn to filters was significant, and clear differences between filters were observed (indicated with different letters in Fig. 2). All eight filter loads for La were significantly different from zero, but for K, only four filters had significant loadings (CA, CN, MCE, PVF), as was the case for Mn (CA, CN, PE, PVF). For Cu and both Zn isotopes, no significant adsorption to filters or differences between filters were found. Because NY belongs to the PA group, one would expect the same results for the NY and PA filter. Apart from La, which has a significantly higher loading on PA, this was indeed the case.

**Speciation and adsorption**

Table 3 gives the relevant chemical species of K, Mn, Cu, Zn, and La in nutrient solution at pH 5.0 as calculated by CHEAQS. The corresponding calculated concentrations of the free metal ion are 49.1 μM for K⁺, 135 nM for Mn²⁺, 0.039 μM for Cu²⁺, 98.6 pM for Zn²⁺, and 11.6 pM for La³⁺. The free ion is, for these metals, quantitatively the most important cationic species. In the case of La, there is one other cationic species in a significant amount, namely La(SO₄)²⁻, with a concentration of 7.6 pM. While K is almost exclusively (99.8%) present in a free cationic form, Cu, Zn, La, and Mn are mainly (86%) present as negatively charged EDTA complexes (Table 3). This could explain why Mn and La show affinities for the same filters (notably PE and PVF), which differ from those to which K adsorbs (Fig. 2). Based on the speciation of Cu and Zn, similar results were expected as for La; however, none of the Cu and Zn filter measurements differed significantly from zero.

To establish the role of the free metal ion in adsorption, different approaches were tried to relate speciation with adsorption. First, we compared sorbed amounts with the amount of free metal ion passing the filter, denoted by the dotted lines in Figure 2. For K and Mn, the sorbed amounts were much lower than the amount of free metal ion passing the filter, but the opposite was true for La on most filters (Cu and Zn showed no significant adsorption). This means that (negatively charged) EDTA complexes of La contribute directly to the observed filter load by adsorption or indirectly by supplying the free ion by dissociation.
Second, the correlation of metal amounts on filters with total metal and free ion concentrations in solution was studied. In evaluating the outcome of such calculations, it must be kept in mind that free ion concentrations have an extra uncertainty introduced by the speciation calculations. The same correlation analyses were made for filter load expressed as charges to study if relationships improved by accounting for mono-, di-, and trivalency of the metals. Both total and free metal concentrations in solution were highly correlated \((r^2 > 0.85)\) with metal load on all types of filters. For PA, no correlation coefficient could be calculated because there were too few data left after the exclusion of two negative values. The highest correlation coefficients \((r^2 > 0.999)\) were observed for cellulose-type filters (CA, CN, MCE) and free metal concentrations. Metal loads on the other artificial polymeric filter types (NY, PC, PE, PVF) correlated best \((0.853 < r^2 < 0.999)\) with total metal concentrations in solution. Figure 3 shows the data for these two groups of filters on a logarithmic scale. The metal load on artificial polymeric filters against total metal concentrations in solution is satisfactorily described by linear regression, but the trend for cellulose filters and free metal concentrations was significantly nonlinear (runs test, \(p = 0.003\)); see also Figure 3. Converting metal amounts on filters to charges on filters weakened most correlations and even made those of the NY filters nonsignificant \((r^2 = 0.49)\).

In Table 4, the metal load on each filter is given as a percentage of the metal amount passing the filter in total moles retained on the filter and in positive charge equivalents. If the metal load on the filter would mainly consist of di- and trivalent metals, then values in the column “positive charges” would be two to three times greater than those in the column “moles.” However, the values in these columns are almost equal (values for NY and PE produced the largest differences, i.e., 1.4 and 1.2, respectively). This shows that monovalent K is almost exclusively responsible for the metal load on the filters because moles correspond almost one to one with positive charge equivalents.

**Discussion**

**Solution composition**

Lanthanum is not a regular component of culture solutions and its addition has consequences for other solution components. The concentration of La itself is very low (10 nM) and direct influences on other medium components are not expected. However, the EDTA concentration of the medium had to be increased from the original 3.76 \(\mu\)M to 5.37 \(\mu\)M to prevent La from precipitating with phosphate \((K_{sp} = 10^{-25.7}\) mol/L at \(25^\circ\)C and \(I = 0\) M [25]). Increasing the EDTA concentration hardly influences the speciation of Cu, Zn, Co, and Fe because they are bound to EDTA for more than 95% already. However, the higher EDTA concentration did change the speciation of Mn. The concentration of free Mn\(^{2+}\) decreased from 0.65 to 0.14 \(\mu\)M and the concentration of MnEDTA\(^{-}\) increased from 0.32 to 0.85 \(\mu\)M. Because both species are still present in a substantial and measurable fraction of the total Mn present, it was considered acceptable. Lanthanum was chosen to represent trivalent metals instead of Fe, which is the only trivalent metal present in the original medium. The reason is that \(^{59}\)Fe, the radioisotope produced during Fe irradiation, is less suitable for low concentration measurements than \(^{140}\)La.

**Adsorption to filters**

It was anticipated that the filters have some cation exchange capacity and thus would electrostatically bind free metals and positively charged complexes [9,13,28]. Figure 3 supports this suggestion for cellulose-type filters. From Table 4, it can be derived from the similarity in values of the columns moles and positive charges that sorption of the monovalent cation K\(^+\) is almost exclusively responsible for the metal load on the

<table>
<thead>
<tr>
<th>Filter type</th>
<th>K</th>
<th>Mn</th>
<th>Cu</th>
<th>Zn(^a)</th>
<th>La</th>
<th>Moles(^b)</th>
<th>Positive charges(^c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cellulose acetate</td>
<td>0.6</td>
<td>0.2</td>
<td>0.4</td>
<td>0.2</td>
<td>0.5</td>
<td>1.4 (\times) 10(^{-9})</td>
<td>1.5 (\times) 10(^{-9})</td>
</tr>
<tr>
<td>Cellulose nitrate</td>
<td>1.6</td>
<td>0.2</td>
<td>0.2</td>
<td>0.01</td>
<td>0.7</td>
<td>3.9 (\times) 10(^{-9})</td>
<td>3.9 (\times) 10(^{-9})</td>
</tr>
<tr>
<td>Mixed cellulose ester</td>
<td>0.4</td>
<td>0.1</td>
<td>0.3</td>
<td>0.1</td>
<td>0.7</td>
<td>8.7 (\times) 10(^{-10})</td>
<td>8.8 (\times) 10(^{-10})</td>
</tr>
<tr>
<td>Nylon</td>
<td>0.01</td>
<td>0.1</td>
<td>0.4</td>
<td>0.6</td>
<td>0.2</td>
<td>2.0 (\times) 10(^{-11})</td>
<td>2.8 (\times) 10(^{-11})</td>
</tr>
<tr>
<td>Polyamide</td>
<td>0.1</td>
<td>—</td>
<td>0.4</td>
<td>0.4</td>
<td>0.5</td>
<td>1.7 (\times) 10(^{-10})</td>
<td>1.7 (\times) 10(^{-10})</td>
</tr>
<tr>
<td>Polycarbonate</td>
<td>0.04</td>
<td>0.1</td>
<td>0.1</td>
<td>0.4</td>
<td>0.1</td>
<td>1.0 (\times) 10(^{-10})</td>
<td>1.1 (\times) 10(^{-10})</td>
</tr>
<tr>
<td>Polyvinylidenefluoride</td>
<td>0.1</td>
<td>0.6</td>
<td>0.6</td>
<td>0.04</td>
<td>1.8</td>
<td>3.3 (\times) 10(^{-10})</td>
<td>3.9 (\times) 10(^{-10})</td>
</tr>
</tbody>
</table>

\(^a\) Data for \(^{60m}\)Zn are used.

\(^b\) Calculated as K + Mn + Cu + Zn + La, negative values excluded.

\(^c\) Calculated as K + 2(Mn + Cu + Zn) + 3La, negative values excluded.

\(^a\) Negative value (see Results).
filters. Furthermore, considering the similarity in La and Mn sorption to the filters, it is hypothesized that di- and trivalent metals bind to specific sites on PE filters or, alternatively, that PE has some affinity for negatively charged metal-EDTA complexes. The highest metal load for Cu (although not significant), of which >99% is associated with EDTA (Table 3), was on the PE filters as well. Our results agree with those of Salbu et al. [29], who found that anions are more prone to sorption on nonionic polymers than cations.

Polycarbonate and NY showed the lowest affinity for metals and are as such recommended for the filtering of culture media and other metal-containing solutions. Furthermore, it is recommended to pre-equilibrate filters in the solution to be filtered and hence saturate possible binding sites [29,30]. Our results are in agreement with those of Wenzel and Wieshaeuser [13] and Wenzel et al. [31], who found that NY membranes had no effect on metal concentrations at pH values between 3 and 5, presumably due to the low cation exchange capacity, and also with Taylor and Shiller [32], who advocate the use of PC filters because of the low surface area. Cellulose-type filters retained the highest metal load (Table 4), which was expected because they can be considered depth filters with a relatively high active surface [30,33]. Winger et al. [12] found that metal concentrations in so-called peepers fitted with cellulose membranes were always lower than in pore waters collected with other techniques. For La, a loss of 5% was reported by Sholkovitz [34] using MCE filters.

Overall, there were significant differences between filters but no significant decreases of metal concentrations in the filtrates (maximum loss for the sum of five metals was 3.5%, PE filter; Table 4). These results have to be considered in view of the filtered volume (5 ml), the total solution composition (only 5 of the 10 metals present were measured), and the solution pH (5.0). Filtering a smaller volume is more likely to produce significant differences in metal concentrations in filtrates because, at equal concentrations, the metal amount passing the filter is smaller. Because membrane filters have a certain saturable capacity to bind cations (cation exchange capacity), the amount of metals that may adsorb is best conceived as an absolute value, independent of filtered volume. Consequently, the loss of metal (species) from solution is more important for small samples, especially when there is too little sample to pre-equilibrate the filter and saturate its capacity. Other nonspiked metals in our solution (Na, Ca, Mg, Co, and Fe) will probably adsorb to filter sites as well, thus contributing to the total metal load, but this was not quantified here.

The relatively low pH of our solution causes considerable competition between protons and metal cations for filter binding sites, thus reducing metal adsorption. Increasing the pH is likely to result in a higher metal load on the filters [13,27] for acidic groups or the filter will deprotonate and become negatively charged. Such an increase of cation exchange capacity with pH was demonstrated for mixed cellulose filters [9] and even for NY filters; significant adsorption of Cu and Pb occurred at pH 6.5 and higher [12]. To assess the role of pH on free metal concentrations, a titration calculation of our solution was performed with CHEAQS, increasing the pH stepwise from three to nine. Because the objective was to study changes in solution complexation, solids were not allowed to form (in this pH range, it would only affect La by formation of LaPO₄). Figure 4 shows that the speciation of K does not depend on pH, but concentrations of Mn²⁺, Zn²⁺, La³⁺, and Cu²⁺ decrease monotonically as pH increases. In short, this means that increasing solution pH will lower free ion concentrations and ultimately removes metals from solution by precipitation; hence, filtration artifacts are expected to be more pronounced at higher pH values. This statement is especially relevant for cellulose filters (see Fig. 3) but may also apply to other filter types (see above).

### Implications for natural waters

The results presented in this article are relevant for natural water sampling because this usually includes a filtration step. Although natural water samples are generally filtered over 0.45 µm, giving the operationally defined dissolved metal concentration [7,8], adsorption phenomena such as described here are primarily related to the filter material and not its pore size. This stems from the fact that our solution contains virtually no particulates but instead only truly dissolved metals. However, pore size will gain importance when, in solution, particles are present that may clog the filter, thereby influencing the effective pore size and flow rate [8]. In addition, it must be noted that the pore size 0.45 µm used to separate dissolved metals has often been questioned [7,8,27] because it still allows for passage of some bacteria [35] and colloids [7,8,34], which are often enriched in metals. Therefore, the use of 0.2-µm membranes is advocated because it reduces the amount of colloids and, more important, it sterilizes the sample, thus preventing the occurrence of microbiologically mediated changes [27]. However, clogging is more likely to occur in 0.2-µm filters than in 0.45-µm filters.

Especially at high pH, small sample volumes, and low metal (species) concentrations, the choice of filter type is a crucial issue. The pH value of water samples depends strongly on sample type (fresh or salt surface water, ground water, soil or sediment pore water, fog water) but ranges at least from 2.3 to 8.3 [9,13], including those pH values for which adsorption is expected to play an important role [27]. Small sample volumes occur, e.g., during collection of sediment pore water by syringe extraction [11] and soil solution extraction [4] and particularly during fog water collection, where samples may be as small as 0.2 ml [5]. Furthermore, filter choice is of major importance when samples are taken for speciation studies, where care must be taken to minimize the influence of filtration on metal solution equilibria. Concentrations of metal species, e.g., the free metal ion, are often in the nM to pM range, while the highest metal amount on a filter measured in this study was already 3.9 nanomoles. This value must, however, be con-
sidered a lower estimate because only 5 of the 10 metals present were measured.

CONCLUSIONS

Differences were shown for the adsorption of K, Mn, and La to different filter types, although no significant decrease in metal solution concentrations was observed. Nylon and PC filters displayed the lowest adsorption capacity for metals and are thus recommended for filtration of metal-containing solutions. Alternately, the highest amount of metals (3.9 nanomoles) was retained by the CN filter. Polyester filters seem to have a higher affinity for di- and trivalent metals and/or their negatively charged metal-EDTA complexes. Furthermore, the free metal ion seems to dominate adsorption to cellulose-type filters, indicating an electrostatic bonding mechanism. Finally, studying metal sorption greatly benefits from the use of complementary tools like radioisotopes and metal speciation calculations.

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