

## ABSTRACT

Th(IV) isotopes are important proxies in oceanographic investigations, and are used as tracers of particle dynamics and particulate organic matter (POC) fluxes out of the euphotic zone through the use of  $^{234}\text{Th}/\text{POC}$  ratios. These approaches rely on empirically determined and variable POC to  $^{234}\text{Th}$  ratios, which might be controlled, in parts, by the abundance of exopolymeric substances (EPS). EPS contain acidic polysaccharides (APS) and are excreted by both phytoplankton and bacteria. To this end, radiotracer experiments with EPS from microbial cultures were conducted to determine the binding environment of  $^{234}\text{Th}(\text{IV})$ -binding ligands in colloids and suspended particles in marine systems. In these experiments, the  $^{234}\text{Th}$  distribution during isoelectric focusing (IEF) and polyacrylamide gel electrophoresis (PAGE) was related to the functional group composition of EPS and of colloidal organic matter (COM) isolated from the Gulf of Mexico (GOM) using cross-flow ultrafiltration. EPS was extracted from phytoplankton (*Emiliana huxleyi* and *Synechococcus elongatus*) and bacteria (*Sagittula stellata* and *Roseobacter gallaeciensis*) cultures by repeated alcohol precipitation. Phosphate and sulfate concentrations were determined using ion chromatography (IC). IEF profiles indicated that 49% to 65% of the  $^{234}\text{Th}$  labeled EPS from plankton and bacteria as well as COM samples from the GOM was found concentrated below pH of 4, near an isoelectric point,  $\text{pH}_{\text{IEF}}$ , of about 2. The carboxylic acid maxima for extracted EPS and COM samples appeared close to the  $\text{pH}_{\text{IEF}}$  of  $^{234}\text{Th}(\text{IV})$ . The phosphate maximum appeared at the same  $\text{pH}_{\text{IEF}}$  as  $^{234}\text{Th}(\text{IV})$  for EPS from *Roseobacter gallaeciensis* and *Synechococcus elongatus*. The sulfate maximum was found at the same  $\text{pH}_{\text{IEF}}$  as  $^{234}\text{Th}(\text{IV})$  for EPS from *S. elongatus* and COM. The molecular weight (MW) of the strongly Th(IV) binding ligand varied from 1-14 kDa, depending on the species, but was about 10 kDa in COM. Thus, depending on the species of plankton or bacteria, the MW and specific functional group composition of the strongly  $^{234}\text{Th}(\text{IV})$ -binding amphiphilic biomolecule can vary. Therefore, different acidic functional groups can, at times, contribute to the binding of Th(IV) to the EPS chelating ligand, which can also have different MWs. This implies that the binding environment for Th(IV), which is present at total concentrations at least a million times lower than the acid functional groups, consists of strong polydentate chelate complexes in clustered structures of carboxylate, sulfates and/or phosphates. The combination of strongly chelating groups and amphiphilicity gives this biomolecule the unique properties of a “sticky” ligand.

