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Distinguishing phosphate from fertilizers and wastewater treatment plant effluents in Western Canada using oxygen isotope measurements

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The successful application of oxygen isotope ratios as a tracer for phosphate in aquatic ecosystems requires that different sources of phosphate are isotopically distinct. The objective of this study was to determine whether the oxygen isotope ratios of phosphate from fertilizers and effluents from wastewater treatment plants in Western Canada are isotopically distinct. Therefore, we carried out oxygen isotope analyses on phosphate in effluent from five different wastewater treatment plants (WWTP) in the Bow River watershed of Alberta, Canada. Samples were collected directly from the final effluent (post-UV) in Banff and Canmore upstream of Calgary, and from effluents of Calgary's WWTPs at Bonnybrook, Fish Creek and Pine Creek. We also carried out oxygen isotope analyses on a variety of phosphate-containing fertilizers that are widely used in Western Canada. Historically, most of the phosphate contained in manufactured fertilizers sold in Alberta came from two distinct deposits: 1) a weathered Pliocene igneous carbonatite located in eastern Canada, and 2) the Permian Phosphoria Formation in the western USA.

Phosphate (PO_4^{3-}) contained in the water or the fertilizer was concentrated and quantitatively converted to pure silver phosphate (Ag_3PO_4). The silver phosphate was then reduced with carbon in an oxygen free environment using a TC/EA pyrolysis reactor linked to a mass spectrometer where $^{18}O/^{16}O$ ratios of CO were measured in continuous flow mode. Preparation of samples for $\delta^{18}O_{PO4}$ analyses was conducted using the Magnesium Induced Coprecipitation (MAGIC) method. Expected oxygen isotope ratios for phosphate in equilibrium with water ($\delta^{18}O_{eq}$) were calculated using the Longinelli and Nuti equation: T (°C) = 111.4 - 4.3 ($\delta^{18}O_{eq}$ - $\delta^{18}O_{water}$).

Measured $\delta^{18}O$ values of phosphate for fertilizer samples varied from 8 to 25 ‰Ȯn average, fertilizer samples of sedimentary origin had higher $\delta^{18}O$ values (15.8%¸) than those of igneous origin (11.5%¸). Phosphate isotopic analyses on samples from WWTP effluents are currently being conducted. We hypothesize that $\delta^{18}O$ values in phosphates of WWTP effluents are controlled by equilibrium oxygen isotope exchange with water. Since water in the Bow River has remarkably low ?^{18}O values ranging between -21 and -18‰ we expect $\delta^{18}O_{eq}$ of phosphate of approximately +4 ‰İf confirmed by ongoing measurements, the $\delta^{18}O_{PO4}$ values for WWTP effluents would be much lower than those of fertilizers. Oxygen isotope compositions of phosphate would consequently be a useful tool to trace phosphate sources affecting riverine systems in Western Canada.