

Comparison of colorimetric analysis, ion chromatography, ICP and DGT for model phosphorus solutions and natural water samples

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Dissolved organic phosphorus in natural water samples is traditionally measured as the difference between total P – measured with colorimetric method (CM) after digestion or ICP – and inorganic P (Pi) – measured with CM or ion chromatography (IC). Determinations performed in this way are however questionable because of possible hydrolysis during measurement, overestimating the Pi fraction. To obtain a better understanding in the analytical methods for P measurement, the malachite green colorimetric method and ion chromatography were compared to total phosphorus measurement by ICP for two different sets of model P compounds and one set of natural water samples.

The first set consisted of 11 model organic phosphorus components and one polyphosphate. In general, neither CM nor IC measured any phosphate for these model organic phosphorus components (less than 4% of total P). However, acetylphosphate and phosphocreatine did hydrolyze during analysis of both IC and CM and 17 up to 100% of the P was detected. We hypothesize that this is explained because of the labile N-P bond for phosphocreatine and the stable resonance form after hydrolysis for acetylphosphate. Phytate, phosphocreatine, ATP, triphosphate and acetylphosphate were also measured using the diffusive gradient in thin films (DGT) technique. After deployment, the adsorbed P on the mixed binding layer was eluted and measured for total P (ICP) and inorganic P (difference of ICP and CM). The measured total P and Pi are given relative to what would be expected to be measured if a Pi solution was subjected to DGT. Only Pi was detected on the ferrihydrite gel for phosphocreatine and ATP for respectively 60% and 30%. This might be due to hydrolysis of the organic molecule prior to adsorption on the ferrihydrite gel or due to hydrolysis during CM measurement since phosphocreatine proved to be labile during this analysis. Triphosphate and glycerolphosphate hydrolyzed partially prior to adsorption on the ferrihydrite gel so that respectively 20% and 4% Pi was detected. Total phosphorus adsorbed on the ferrihydrite gel accounted for respectively 48% and 54%. Phytate was not able to adsorb on the ferrihydrite gel and was not measured after DGT deployment.

Next, the analysis of an Pi/ferrihydrite solution - a model colloidal P solution - was performed using CM and IC and compared to total P (ICP). Up to 80% of the colloidal bound P can still be measured using the CM because of the acid environment during the analysis. Measurements with IC of colloidal bound P were below detection limit.

In a final experiment, the CM, IC and ICP results were compared for 120 natural water samples obtained from rivers, ditches, drainage tubes and ground water. On average, the CM and IC measured respectively 95% and 77% of the total P (ICP). The difference in these results can be explained by the presence of colloidal P or P associated with Fe or Al, which in turn are part of an organic molecule. For this set of 120 natural water samples, the malachite green CM appears to be a better measure for total P instead of Pi.