# Improved Wastewater Treatment & Mill Performance with new COD **Monitoring Technology**

Stephanie Horner<sup>1</sup>, Robert Menegotto<sup>1</sup>, Pauliina Tukianien<sup>2</sup>, Antti Grönroos<sup>2</sup>, Marjatta Piironen<sup>3</sup>, Sakari Halttunen<sup>3</sup>, liris Joensuu<sup>3</sup>, Serge Genest<sup>4</sup>, Brian O'Connor<sup>4</sup> <sup>1</sup>MANTECH, Canada, <sup>2</sup>VTT, Finland, <sup>3</sup>Kemira, Finland, <sup>4</sup>FPInnovations, Canada

### Introduction

Pulp and paper mills produce a large volume of wastewater and residual sludge, which is a growing concern due to increasing environmental regulations becoming more strict. Experts are looking for solutions to reduce their freshwater intake and ultimately achieve close to zero liquid discharge. The challenges of these solutions include: high organic concentrations in production and wastewater effluent, operation costs, performance, and impacts to the environment. Additionally, the push for stricter COD effluent discharge regulations suggests a safer, faster and more robust COD monitoring tool is essential for process optimization and discharge compliance.

Since mid-2013, the peCOD method has been proven and trusted as a green, safe, fast and accurate alternative to the COD<sub>cr</sub> method for a kraft Chilean mill. The 15 minute peCOD results led to a reduction in hypochlorite used for bleaching, with no loss of product quality. This has resulted in lower organics in the waste water plant and further reductions of chemicals and energy used for treatment. The total savings over 12 months netted \$3 million dollars (US), a 3-day return on investment for the peCOD unit. The strong COD<sub>cr</sub> to peCOD correlation at the Chilean pulp and paper mill was reinforced with a range of effluents from both kraft and mechanical pulp mills in this project.

#### Methods

The peCOD method eliminates the use of mercury, dichromate, and concentrated acid, which are found in the  $COD_{cr}$  method. The core of the peCOD nanotechnology utilizes the high oxidation potential of UV irradiated TiO<sub>2</sub> nano-particulates to fully oxidize all present species. The peCOD measures soluble COD (sCOD), therefore suspended solids of >50 µm are removed prior to sample analysis. The testing range is 0.7mg/L-15000mg/L of COD, though incorporating dilution can extend this range.

There were two peCOD configurations utilized in this project, automated L100 and online P100. Both use the same peCOD technology and consumables, but are setup to operate under different conditions.

Figure 1: PeCOD configurations utilized during study. From left to right: laboratory L100, automated L100 and online P100 peCOD.







#### Results

The peCOD and COD<sub>cr</sub> tests conducted on pulp and paper mill effluents, at Kemira<sup>3</sup> and FPInnovations<sup>4</sup> laboratories, displayed strong correlation with r<sup>2</sup> values ranging from 0.92-0.99 on both peCOD configurations. The results below from Kemira<sup>3</sup> (Figure 2) showcase an r<sup>2</sup> of 0.997 between an automated L100 peCOD and COD<sub>Cr</sub>.

FPInnovations<sup>4</sup> had similar results to that of Kemira<sup>3</sup> including successful experimentation with the online P100 peCOD configuration. The comparison of peCOD results between the automated L100 and online P100 is illustrated in Figure 3. This reinforces that suspended solids do not contribute to the total COD. Experiments confirmed that the solid contribution to the total COD concertation was an insignificant 0 - 4 %. On average, where differences existed, peCOD reported slightly higher COD results than  $COD_{cr}$ . This is potentially due to the peCOD more effectively oxidizing recalcitrant COD present in treated effluent samples.

Figure 2: Automated L100 peCOD versus filtered (0.45 µm) COD<sub>cr</sub> for multiple sampling locations of a thermomechanical pulp and paper mill.

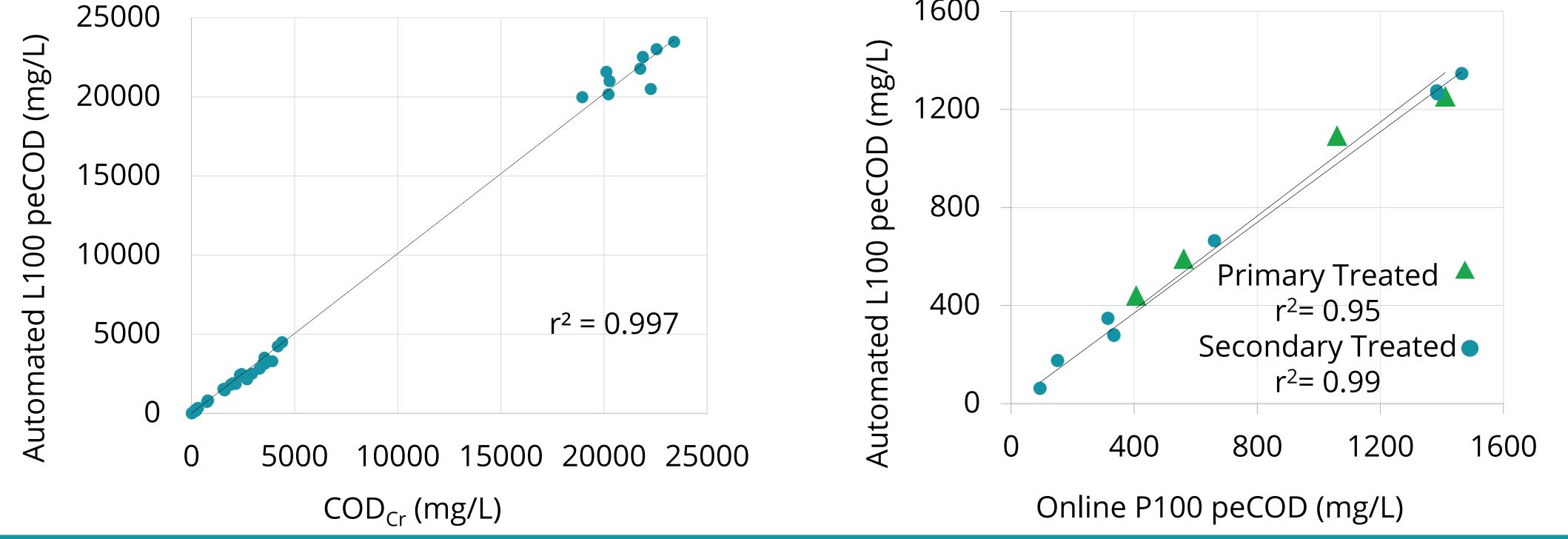
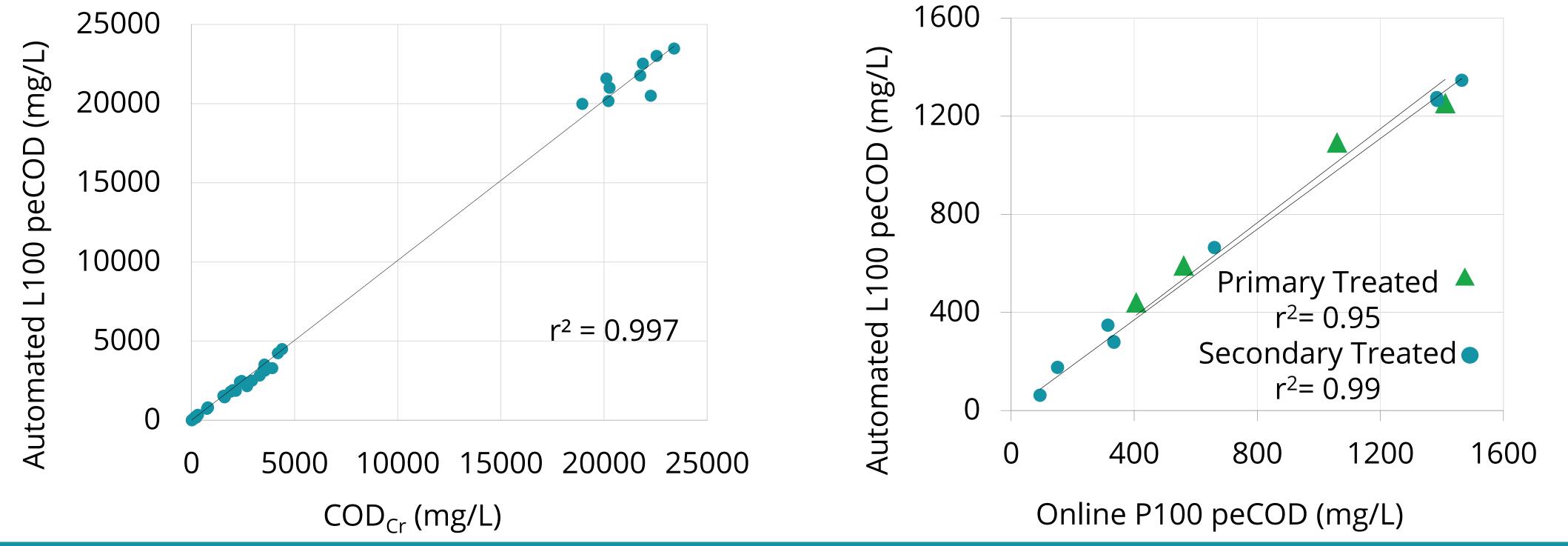


Figure 3: Comparison of automated L100 peCOD and online P100 peCOD for primary (green triangle) and secondary (blue circle) treated kraft mill effluents.



## Conclusions

The peCOD method has been proven as a safe and effective COD monitoring tool in effluent treatment process improvement and process optimization in pulp and paper mills. The strong correlation between peCOD and  $COD_{cr}$ suggests it could be used as an online monitoring tool for in-mill operation and wastewater treatment optimization. Its green and safe technology will also protect laboratory professionals, public health and the environment.

