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Performance evaluation of a correlation-based spectroscopic method for ammonia equivalents in sewers and WWTP influents

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Abstract

Ammonia monitoring in wastewater is essential for environmental protection and process optimization, yet traditional methods are costly and maintenance-intensive. This study evaluates the potential of in-situ UV/Vis spectrometers for monitoring ammonia equivalents in sewers and WWTP influents, which has been overlooked in literature. We assess three calibration approaches—multiple linear regression, partial least squares, and random forest—across two catchments in Switzerland. Initial results show promising predictive performance (R^2 of best performing models between 0.6 and 0.8). Wavelength importance analysis shows a clear reliance on UV wavelengths for ammonia predictions.

Highlights

- We explore UV/Vis spectrometers for NH_4-N monitoring, despite its lack of UV/Vis absorption.
- Calibration test results show PLS, MLR with a performance (R^2) between 0.6 and 0.8.
- UV wavelengths are particularly important for ammonia predictions.

Introduction

Ammonia monitoring is critical for protecting aquatic ecosystems, ensuring regulatory compliance, and optimizing wastewater treatment. Traditional ammonia monitoring methods (e.g., wet chemical analyzers, ion selective electrodes) come with high acquisition and maintenance costs and present operational challenges in raw wastewater due to interference from complex wastewater matrices (e.g., suspended solids, fats, oils, grease, interfering ions). UV/Vis spectrometers that have been successfully employed for monitoring other relevant wastewater parameters (e.g., TSS and COD) using a wide range of calibration methods (Lepot et al., 2016), offer a promising alternative.

This study builds on previous research demonstrating the ability to track ammonia trends in raw wastewater with an in-situ UV/Vis spectrometer (Pacheco et al., 2020). We expand on this by evaluating sensor performance across multiple catchments, testing different calibration models (both linear and non-linear machine learning), and employing methods to reveal spectral importance.

Methodology

Study sites

We deployed the ISA spectrometer (GO Systemelektronik GmbH, Germany) at a total of three locations. Table 1 summarizes the relevant information of these sites along with catchment and reference measurement information. At the measurement site VH, the sensor was installed in a flume through which raw wastewater from a nearby sewer was pumped and was operated nearly continuously over the duration of a 6 month monitoring campaign (Lechevallier et al., 2024). At the measurement site AVA, the sensor was installed at the WWTP Altenrhein after primary treatment. Unfortunately, due to chemical dosing in primary treatment in combination with the pressurized air cleaning of the sensor's measurement windows, mineral deposits formed on the measurement windows, severely compromising the quality of the spectral measurements. Despite adaptations to the cleaning regimen, data quality from this site could not be ensured. Therefore, this study site was excluded from further analysis. At the WWTP Werdhölzli (measurement site ERZ), the sensor was installed along with other sensors in a metal flume between primary and secondary treatment.

Table 1: Sites at which the Gosys ISA Spectrophotometer was installed, with corresponding catchment information and number and method of NH4-N reference measurements. Due to poor data quality, data collected at monitoring site AVA was not further processed for model building.

Monitoring site			Catchment information		NH_4-N reference measurements	
ID	Name	Location	PE	Wastewater	Method	# of samples
VH	Versuchshalle Eawag	Dübendorf (CH)	25 000	Mixed	Flex / Lachat QC8500: Ion chromatography	471
AVA	WWTP Abwasser-verband Altenrhein	Altenrhein (CH)	83 000	Mixed	Endress+Hauser: Ammonium Analyzer CA80AM	300+
ERZ	WWTP Werdhölzli	Zürich (CH)	670 000	Mixed	Hach Ammonium Analyzer NH6000sc	5000+

Sensor and reference measurements and preprocessing

The sensor measures the wastewater absorbance in the range form 200 nm to 706 nm at a spectral resolution of 2 nm. The ISA spectrometer has an adjustable optical path length that was calibrated locally at each monitoring site to obtain spectral measurements that are within the sensor's range. According to the sensor manufacturer, absorption measurements at wavelengths below the absorption maximum must be discarded due to absorption of the optical cable in the UV range. Thus, measurements before the absorbance peak are not reliable. This peak was determined to be at 235 nm. Thus, we are left with a spectrum in the range of 236-706 nm.

NH4-N reference measurements were taken with different methods at each site (see Table 1). At VH, reference samples were taken either manually or with an automatic sampler and analyzed via ion chromatography. At ERZ an ammonium analyzer (NH6000sc, Hach, USA) was installed and measured NH4-N roughly every 20 minutes. The performance of the ammonium analyzer was validated through regular manual laboratory measurements through the WWTP staff.

Sensor calibration

The ISA spectrometer requires a local calibration to reference observations. For sensor calibration we assess three different calibration methods: multiple linear regression (MLR), partial least squares (PLS), and random forest (RF). For MLR model building, we considered combinations of four wavelengths. Among all possible combinations of four wavelengths between 236 and 706 nm (in steps of 2 nm), 10,000 random combinations were tested to determine the best performing combination. For PLS model building the number of components was tuned with cross-validation and determined to be 5 components. RF model hyperparameters were similarly tuned with 10-fold cross-validation.

A critical aspect of sensor calibration is ensuring that the selected spectral measurements and corresponding target values represent the full range of local wastewater pollution variability. To achieve this, we avoided random sampling and instead applied k-means clustering to group samples with similar feature and target characteristics. An equal number of calibration samples was then drawn from each cluster to ensure balanced representation across the dataset.

Wavelength importance

Wavelength importance analysis of calibrated models was performed differently depending on each calibration method. For the MLR model, we quantified wavelength importance by determining the relative number of times each wavelength appeared in the best 1000 performing models (i.e., relative selection frequency). For the PLS model, variable importance in projection (VIP) scores were used to assess the contribution of each wavelength to the model's predictive performance. For the RF model, permutation importance was computed by randomly shuffling each wavelength and measuring the resulting decrease in model accuracy, with larger decreases indicating higher importance.

Results and discussion

Model performance and calibration data requirements

We evaluated model performance as a function of calibration sample size and calibration method at both monitoring sites. Figure 1 shows how the test set performance (measured as mean absolute percentage error (MAPE)) changes when increasing the number of training samples from 20 to 100. In this range, both MLR and PLS models consistently outperformed the RF model, achieving higher predictive accuracy and lower variance. While the linear models showed only marginal improvements with more calibration samples, their performance became increasingly stable, as indicated by the reduced variability across cross-validation folds. The RF model, by contrast, performed poorly with limited data and did not reach the accuracy of the linear models within the tested range. However, when the training set size was increased to 80% of the available data, its performance improved substantially and approached that of MLR and PLS, underscoring its higher calibration data requirements.

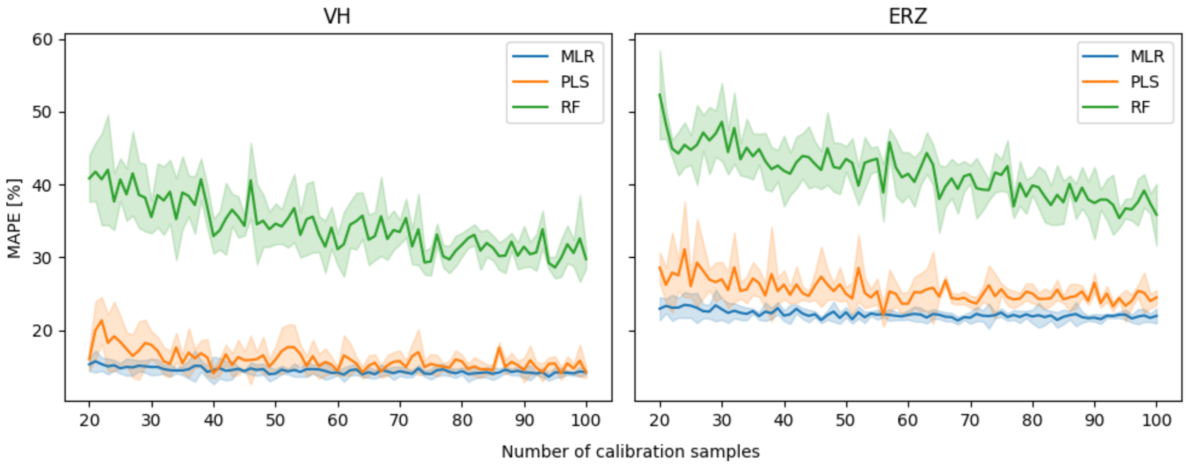

Figure 1. Model performance (MAPE) on test set as a function of the number of training samples for the three tested calibration techniques. The shaded region represents the variance of model performance (standard deviation) across 10-fold cross validation.

Figure 2 further compares model performance using a fixed set of 50 calibration samples, selected equally from k-means–generated clusters, with model predictions evaluated on the remaining data. In this setup, MLR and PLS again demonstrated solid performance, particularly at site VH ($R^2 \geq 0.8$) and moderately at ERZ ($R^2 \geq 0.6$), in line with previously reported results (Pacheco et al., 2020). The RF model, however, showed weak predictive power, consistent with its observed need for larger calibration sample sizes. These results confirm that linear models can be effective even with relatively small, well-selected calibration sets, while nonlinear models like RF require substantially more data to generalize reliably.

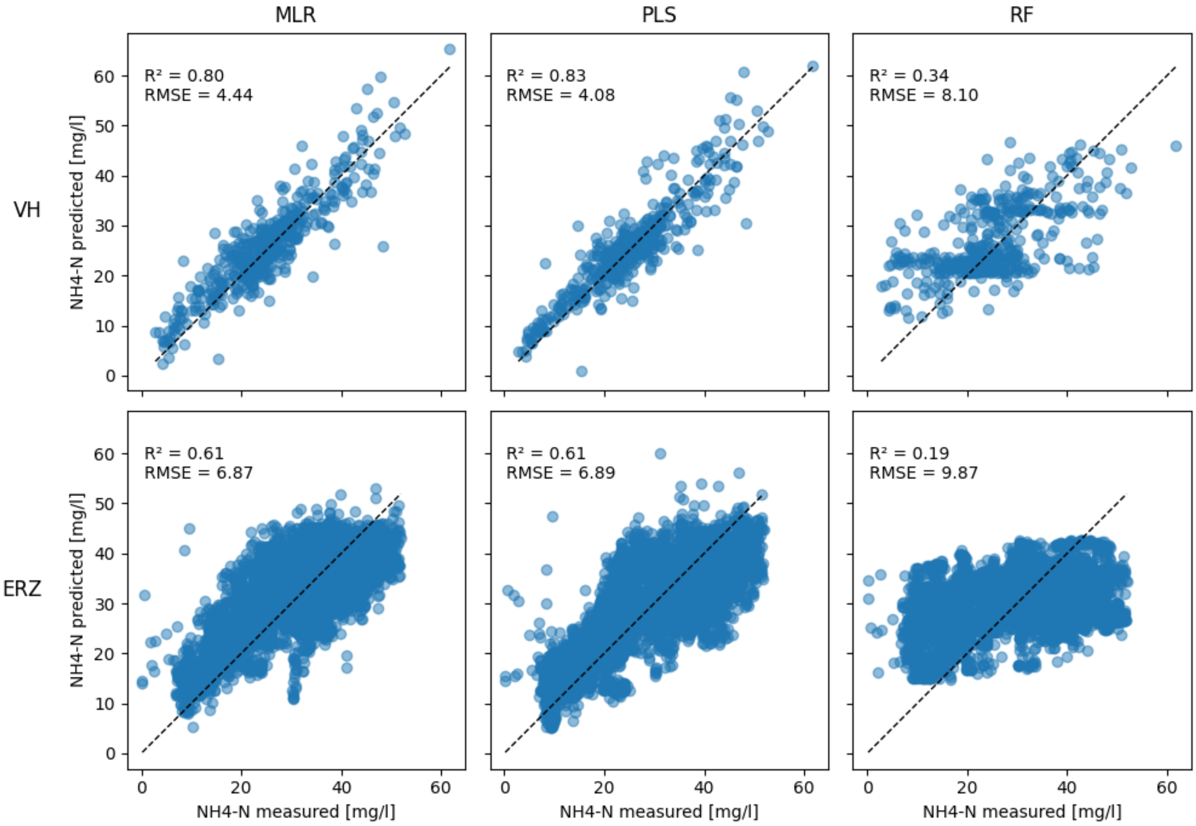

Figure 2. Model predictions on a test dataset using MLR, PLS and RF models calibrated on 50 samples selected equally from k-means generated clusters.

Wavelength importance

To investigate which spectral regions contribute most to model predictions, wavelength importance was assessed separately for each model using method-specific metrics: relative selection frequency for MLR, VIP scores for PLS, and permutation importance for RF. Each model's importance metric was plotted across the wavelength range for both locations (see Figure 3). All three models consistently identified the UV range as the most important spectral region, indicating its relevance for predicting NH_4-N equivalents. Since ammonia shows little absorbance in the UV range, other correlated wastewater constituents with stronger UV absorbance may be leading to the importance attributed to the UV range. However, organic pollution levels measured during the campaigns (DOC at VH and TOC at ERZ) show only weak correlation to ammonia measurements, so at this point we cannot determine which constituent is responsible for this effect. Differences in the attributed wavelength importance emerged in non-UV wavelengths. For example, the PLS model shows elevated VIP scores around 420 nm for the ERZ location, a pattern not reflected in the MLR or RF models.

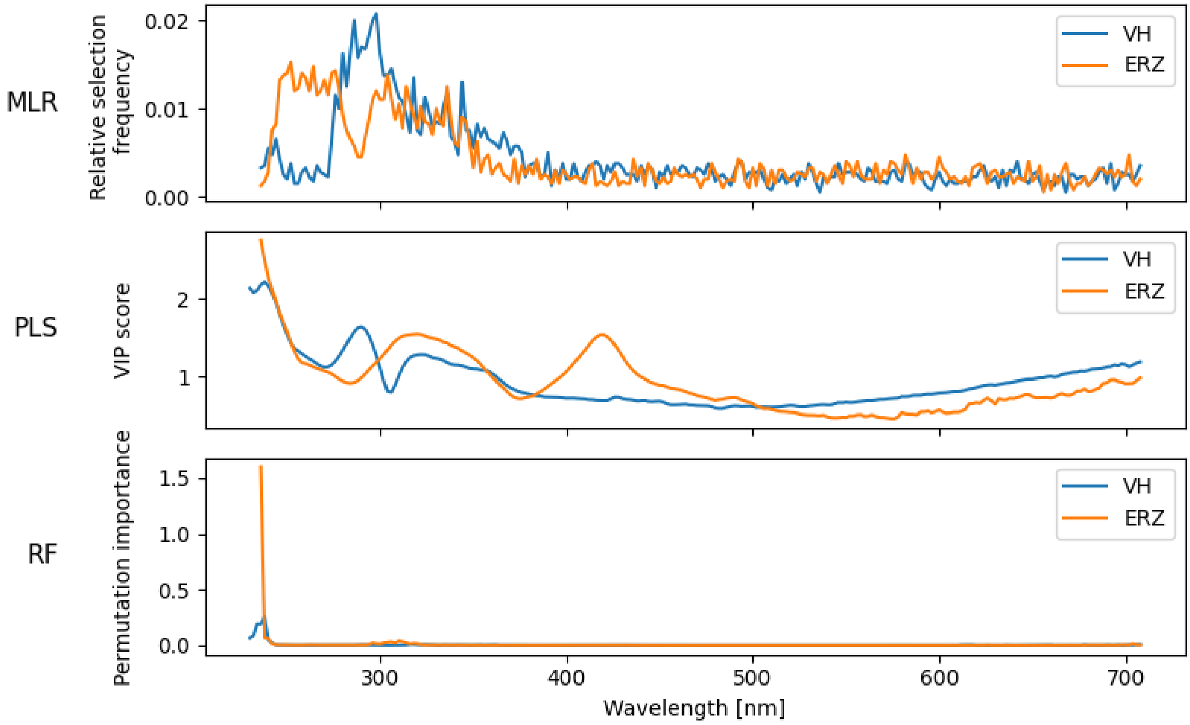

Figure 3. Wavelength importance for the three investigated calibration techniques and both locations. All models attribute strong importance to the UV range.

Conclusions and future work

We see potential in the use of UV/Vis spectrophotometers for indirect ammonia monitoring in wastewater systems. However, model performance appears to be highly site-specific. Given that ammonia itself exhibits minimal absorbance in the UV/Vis range (Chen et al., 2019), spectroscopic predictions of ammonia must rely on correlations with other absorbing constituents that covary with ammonia concentration. The wavelength importance analysis highlights the central role of the UV region, supporting this correlation-based interpretation.

To improve model robustness, future work should attempt to identify the UV absorbing constituents that correlate with ammonia across time, treatment stages, and catchments. Comparing wavelength importance across multiple parameters may reveal overlapping spectral signatures that could inform more mechanistically interpretable models. Ultimately, identifying the conditions under which spectroscopic ammonia measurements are reliable, and more importantly when they are not, is critical for their operational deployment.

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