RAMAN SPECTROSCOPY AND FUSION CLASSIFICATION TO IDENTIFY PLASTIC RECYCABLES TARGETING MICROPLASTICS

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Abstract

Identification of plastic type for microplastic particles (size range of 0.001 mm – 5 mm) is vital to understand the sources and consequences of microplastics in the environment. Fourier-transform infrared and Raman spectroscopy are two dominating techniques used to identify microplastics. The most common method to identify microplastics with spectroscopic data is library searching, a process that utilizes search algorithms against digital databases containing spectra of various plastics. Presented in this study is a new method to utilize spectroscopic data called fusion classification. Fusion classification consists of merging multiple non-optimized classification methods (classifiers) to assign samples into categories (classes). The purpose of this study is to demonstrate the applicability of fusion classification to identify microplastics..

Objective

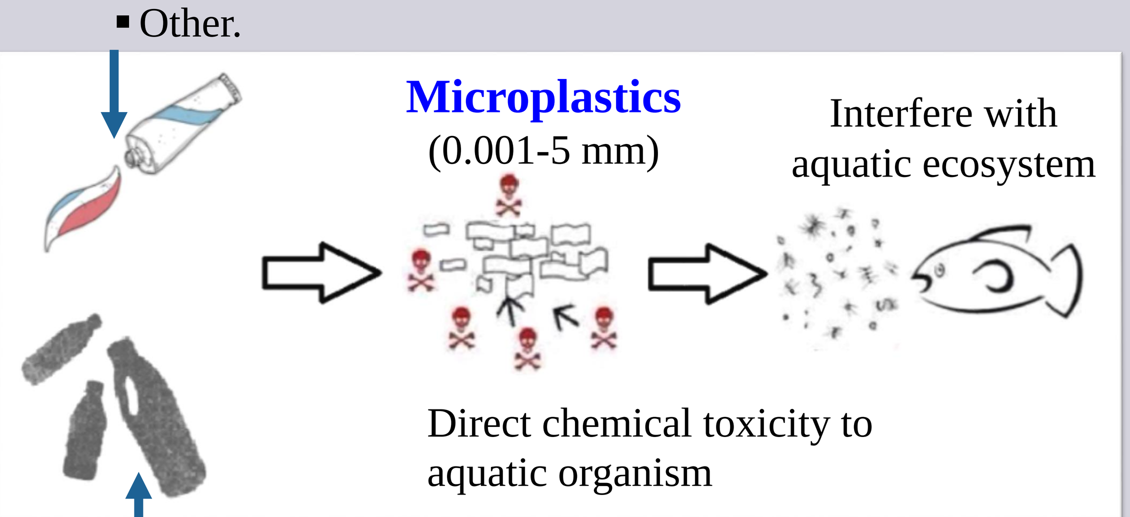
- Identify plastic recyclables using fusion classification to improve microplastic identification accuracy

Background

- > 4.5 billion metric tons of plastic produced in 2015.
- 36.2 billion metric tons projected by 2050.
- 4.8 – 12.7 million metric tons enter the ocean annually.

Primary Source

- Intentionally engineered:
  - Microbeads used in cosmetic products.
  - Other.



Secondary Source

- Consequence of:
  - Photolytic, mechanical, thermal and biological degradation of any plastic goods.

Limitations of Spectroscopic Analysis

- Interference of spectroscopic data caused by:
  - Sediments
  - Degree of degradation
  - Additives such as dyes, antioxidants, etc.

Spectroscopy

- **Library Matching (Common method)**
- **Fusion Classification (New method)**

Approach

Fusion Classification

- Assigning a sample to a category (class) using classification methods (classifiers).
- 17 classifier used in order to:
  - Reduce risk misidentification.
  - Improve classification accuracy.
  - Overcome limitations of stand alone classifiers.

Table 1: Classifiers

Classifiers with Tuning Parameter	Classifiers with No Tuning Parameter
Mahalanobis distance (MD) Q-residual (Qres) Sine Divergence criterion (DC) Partial least squares discriminant analysis (PLS2-DA) k nearest neighbor (kNN)	Euclidean distance Procrustes analysis unconstrained (PA) Inner product correlation Determinant Procrustes Analysis constrained (PA[a]) Cosine Extended inverted signal correction difference (EISCD)

Classifiers with Tuning Parameter

- Tuning parameter based on a number value:
  - PLSDA - latent variables (LVs)
  - kNN - number of nearest neighbors
  - MD, Qres, DC, and Sine – eigenvectors

Classifiers with No Tuning Parameter

- Determine the degree of similarity for a target sample compared to each class mean.
- Threshold selection required.

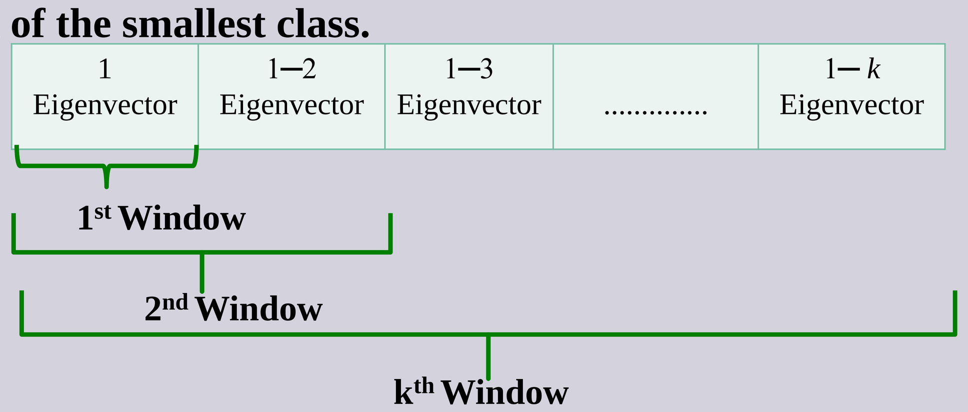
Our Method

- No training (optimization) , weights, or threshold selection of each classifier:
  - Uses raw values.
- Optimization based on a window of respective tuning parameter values:
  - Simplifies classification ensemble

Tuning Parameter Window Selection

- Rule of thumb;
  - 99% information of class (**X**) is captured.
  - LVs and eigenvectors are not excessively composed of noise.
  - Maximum window size is based on the rank (k) of smallest class

Example: Eigenvector based single classifier. Where *k* is the rank of the smallest class.



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Fusion Rule: SUM

- Values normalized to unit length.
- Samples assigned to class with lowest sum.

Classifier

- 1—5 PlS2-DA
- 6—10 kNN
- 11— 5 MD
- 16—20 Sinθ
- 21—25 Q-res
- 26—30 DC
- 30 — 41 Non-traditional classifiers

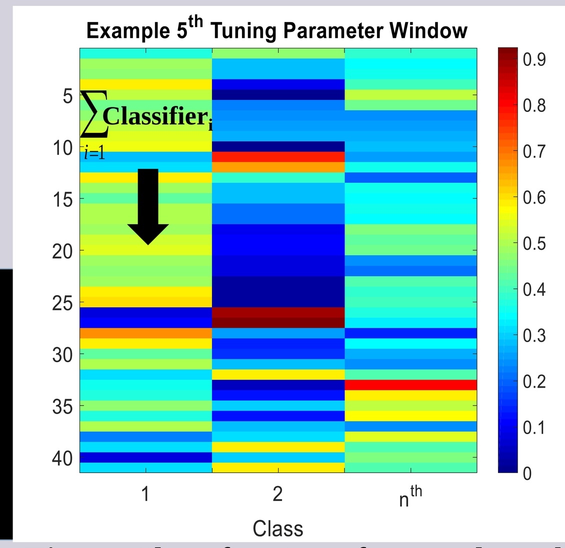

Fig. 1: Classification of a sample at the 5th tuning parameter window

% Performance Parameters

	Belong to Class	*Does not belong to Class*
Positive Result	**True Positive (TP)**	**False Positive (FP)**
Negative Result	**False Negative (FN)**	**True Negative (TN)**

$$\%Accuracy = \frac{TP+TN}{TP+TN+FP+FN} \times 100$$

$$\%Sensitivity = \frac{TP}{TP+FN} \times 100$$

$$\%Specificity = \frac{TN}{TN+FP} \times 100$$

Experimental Design

Table 2: Sample information breakdown103 samples and 188

Class #	Plastic Types	# of Samples	# of Spectra
1	Polyethylene Terephthalate (PET)	28	40
2	High density polyethylene (HDPE)	23	38
3	Polyvinyl chloride (PVC)	4	17
4	Low density polyethylene (LDPE)	18	28
5	Polypropylene (PP)	11	28
6	Polystyrene (PS)	19	37

Allen, V., Kalivas, J. H., & Rodriguez, R. G. (1999). Post-Consumer Plastic Identification Using Raman Spectroscopy. *Applied Spectroscopy, 53*(6), 672-681.

Data Sets

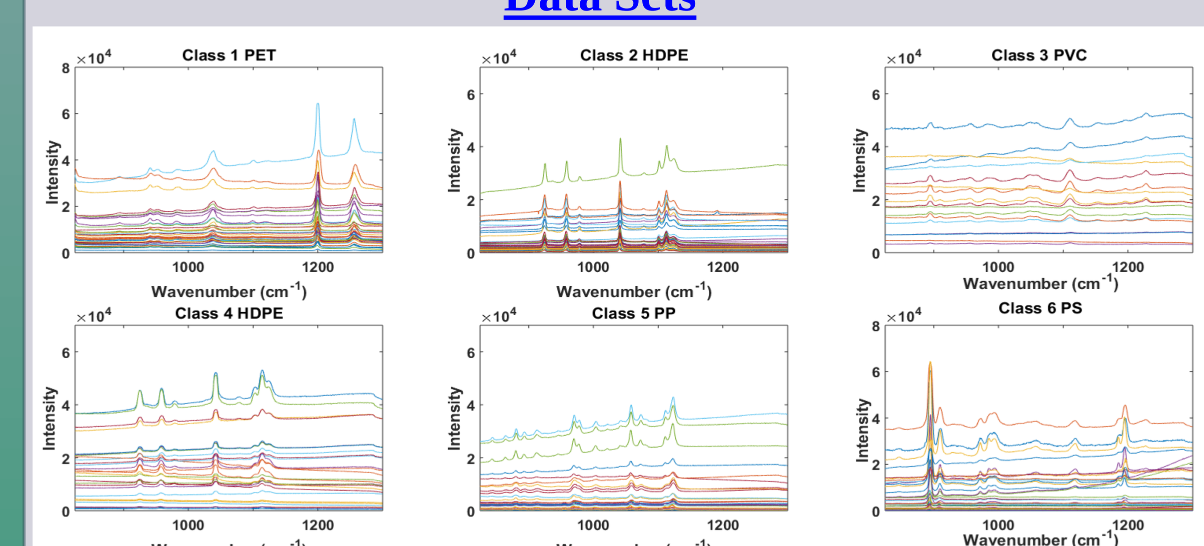

Fig. 2: Raman spectral data for each plastic type i.e. PET, HDPE, PVC, HDPE, PP and PS.

Results

Table 3: Overall (188) library matching results

% Performance Parameter	No Threshold	Threshold Cos θ ≥ 0.70	0.75	0.85	0.90
Accuracy	96.3	92.3	89.9	58.7	0
Sensitivity	96.4	85.8	81.7	41.6	0
Specificity	50	100	100	100	0

- Comparing fusion to frequently used stand alone classifiers

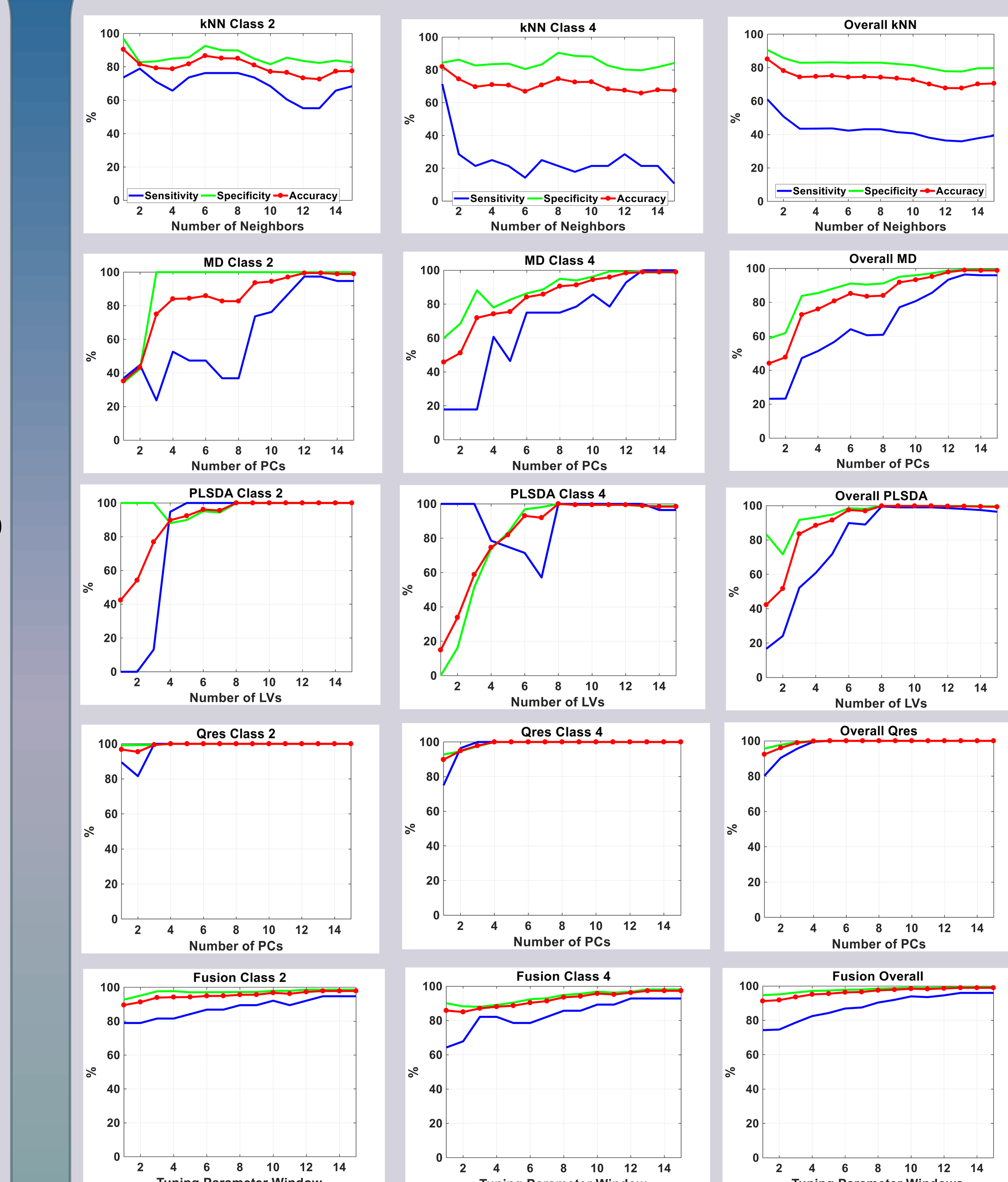

Fig.2: Each figure shows accuracy (red), sensitivity (blue) and specificity (green)

Conclusion

Library Matching	Fusion Classification
Threshold selection: • Value is subjective • Too high— risk not identifying samples. • Too low— risk misidentification of samples.	No threshold selection for individual classifiers: • Simplifies classification. • Window size is used instead based on; • Class with lowest rank. Higher accuracy, sensitivity and specificity than standalone classifiers: • Reduces the risk of misclassifying abnormal samples. Identification is based on available classes.

Future Work

- Apply fusion classification to identify;
  - Physically degraded colored microplastic using Micro-Raman and Micro-FTIR.
  - Microplastic particles in the Snake river

Acknowledgement

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