Review

# Surface Enhanced Raman Spectroscopy in environmental analysis, monitoring and assessment

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HIGHLIGHTS

- Surface Enhanced Raman Spectroscopy (SERS) based environmental analysis is assessed.
- Reported limits of detection of a range of pollutants are collated and summarised.
- SERS can potentially match mass spectrometry in terms of sensitivity.
- Increasing reproducibility of SERS techniques is important for future applications.
- An overview of the key challenges and potential solutions is provided.

GRAPHICAL ABSTRACT
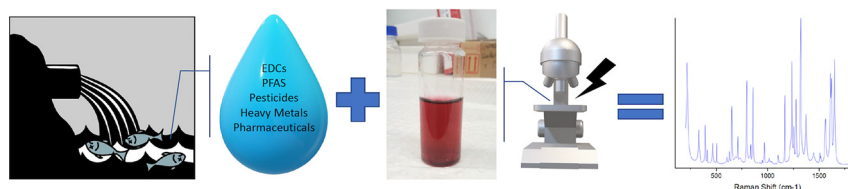
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ABSTRACT

Environmental pollution is usually monitored via mass spectrometry-based approaches. Such techniques are extremely sensitive but have several disadvantages. The instruments themselves are expensive, require specialized training to use and usually cannot be taken into the field. Samples also usually require extensive pre-treatment prior to analysis which can affect the final result. The development of analytical methods that matched the sensitively of mass spectrometry but that could be deployed in the field and require minimal sample processing would be highly advantageous for environmental monitoring. One method that may meet these criteria is Surface Enhanced Raman Spectroscopy (SERS). This is a surface-sensitive technique that enhances Raman scattering by molecules adsorbed on rough nanostructure surfaces such as gold or silver nanoparticles. SERS gives selective spectral enhancement such that increases in sensitivity of 10^{10} to 10^{14} have been reported. While this means SERS is, theoretically at least, capable of single molecule detection such a signal enhancement is hard to achieve in practice. In this review the background of SERS is introduced for the environmental scientist and the recent literature on the detection of several classes of environmental pollutants using this technique is discussed. For heavy metals the lowest limit of detection reported was 0.45 µg/L for Mercury; for pharmaceuticals, 2.4 µg/L for propranolol; for endocrine disruptors, 0.35 µg/L for 17β-estradiol; for perfluorinated compounds, 500 µg/L for perfluorooctanoic acid and for inorganic pollutants, 37g/L for general pesticide markers. The signal enhancements achieved in each case show great promise for the detection of pollutants at environmentally relevant concentrations and, although it does not yet routinely match the sensitivity of mass spectrometry. Further work to develop SERS methods and apply them for the detection of contaminants could be of wide benefit for environmental science.

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Contents

1. Introduction

The traditional (and very effective) method to detect micro-pollutants in the environment is to use chromatography as a separation step followed by mass spectrometry (ideally high-resolution) for detection. Liquid Chromatography – Mass Spectrometry (LC-MS) and Gas Chromatography – Mass Spectrometry (GC–MS) are the two most widely used techniques. Both GC–MS and LC–MS have high sensitivity (down to ng/L levels or lower) but the instruments themselves are complex and require a high degree of specialized training to use and maintain. Extensive sample pre-treatment is also usually required prior to analysis. This means that both GC–MS and LC–MS are costly and time consuming to use for high throughput analysis and unsuitable for real-time monitoring in the environment. A method that could detect target compounds faster and with minimal sample preparation would thus be highly advantageous. One such method is Raman Spectroscopy. Although by itself this technique cannot match mass spectrometry for sensitivity the use of Surface Enhanced Raman Spectroscopy (or SERS) may allow circumvention of this problem.

Briefly, SERS is a spectroscopic technique that relies on electronic and chemical interactions between the excitation laser of the spectrometer, the analyte of interest, and a particular substrate to selectively boost the signal, and thus detection, of target molecules. Among the wide variety of available SERS substrates, colloidal metal (usually gold- or silver-based) nanoparticle systems are the most widely used due to their effectiveness, ease of preparation of the nanoparticles, and the ability to tune analytic sensitivity through chemically-controlled variation of nanoparticle type and size (Tian et al., 2014). Raman Spectroscopy requires comparatively little pre-treatment of samples and is quick to perform, with measurement times being on the scale of seconds to minutes compared to tens of minutes (and in some cases hours) for conventional, chromatography-mass spectrometry-based methods (Jones et al., 2003). This means SERS is able to boost signal detection by as much as 10^{10} or 10^{14} in a similar time frame as standard Raman, with single molecule detection being theoretically possible. In practice single molecule detection is very hard to perform outside very specific laboratory set ups but SERS is still increasingly widely used for its high sensitivity, fast analysis time (with minimal sample preparation), and the fact that it is amenable to many different target compounds, including pollutants.

SERS can potentially not only save a significant amount of time and money in environmental detection but also allow remote and automatic sampling of water sources on a large scale (Halvorson and Vikesland, 2010). Several obstacles remain to be overcome before this can become routine however, not least of which is how to improve reproducibility of measurements at low concentrations from real world samples as opposed to lab studies.

This review aims to provide an overview of the current state of SERS in the field of environmental pollutant detection. The contaminant types covered are heavy metals, pharmaceuticals, hormonal and endocrine disrupting compounds, perfluorinated compounds (such as Per- and Polyfluoroalkyl Substances - PFAS), and pesticides. An assessment of current strengths and weaknesses in using SERS for environmental research and recommendations for further research are also presented.

2. Background

2.1. Raman spectroscopy

Raman Scattering was first discovered in 1928 when C.V. Raman and K.S. Krishnan observed the phenomenon of a second type of light scattering in addition to the already known Rayleigh scattering (Raman and Krishnan, 1928). Raman and Krishnan proposed that this new scattering process was informative about the excited state of any particular molecule (Raman and Krishnan, 1928). Raman was awarded the 1930 Nobel Prize in Physics for this discovery (which was named after him) but even he could not have predicted the wide range of applications his method would eventually contribute to.

Raman spectroscopy utilises inelastic scattering (or Raman scattering) of light to excite a particular analyte and measures the resulting molecular vibrational modes (McNay et al., 2011). The bulk of the Raman scattering effect can be described as the shift in energy by a molecule from a ground vibrational state to an excited state via an incident photon to the molecule. This is known as Stokes Raman scattering (Smith and Dent, 2005). When a molecule existing in an excited state, often due to thermal energy, scatters to a ground state and energy transfer is from the molecule to the scattered photon this is known as Anti-Stokes Raman scattering (Smith and Dent, 2005). Both types of Raman scattering have their uses however at room temperature where only a small number of molecules can be expected to be in an excited state Stokes Raman scattering is the predominant phenomenon occurring.

Because the various vibrational modes of a particular molecule are dependent on molecular structure, a distinct advantage of Raman spectroscopy is that it is sensitive to both the molecular structure and chemical composition of the analyte, thus being it is able to provide a unique "fingerprint" for any chemical compound (Kudelski, 2008). This property is extremely useful.

Raman spectroscopy measurements are typically simple to perform and are non-invasive and non-destructive, Measurements can be taken through transparent glass, water and even plastic (Smith and Dent, 2005). Raman is almost insensitive to water, enabling efficient measurements of biological and environmental samples in a way that is hard to do with related techniques such as infrared spectroscopy. As a result

Raman spectroscopy is today used in a wide variety of fields and applications including material science and medicine (Kudelski, 2008; McNay et al., 2011). The major weakness of Raman is that since relatively few photons are scattered it gives inherently weak signals and this reduces the effectiveness of the technique for environmental monitoring. Specialist methods can however, be used to improve signal intensity. The discovery of SERS (Surface Enhanced Raman Spectroscopy) in the 1970s in particular has been a major driver in this regard.

2.2. Surface Enhanced Raman Spectroscopy (SERS)

SERS was first observed in 1974 (Fleischmann et al., 1974). It is a surface-sensitive technique that relies on electronic and chemical interactions between the excitation laser, analyte of interest, and a SERS active substrate (usually gold or silver surfaces or nanoparticles) to selectively enhance Raman scattering and so boost signal detection of the target molecule (Fleischmann et al., 1974). The boost in signal detection has been reported to typically be 10^4–10^6 (Kandjani et al., 2014) with increases in the order of 10^{14} being possible (Kneipp et al., 1999). While this theoretically means SERS is capable of single molecule detection such a signal enhancement is hard to achieve in practice (although even the smaller signal enhancements achievable with minimal sample processing show great promise in a variety of areas, including environmental science). An illustration of SERS is given in Fig. 1.

The mechanisms behind the SERS phenomenon are not fully understood but are perhaps best explained by electromagnetic theory (Etchegoin and Le Ru, 2010). This posits that an electromagnetic enhancement process occurs when the target analyte adsorbs onto a metal surface and causes an interaction with the surface plasmons - which are localised coherent oscillations of electrons on a surface which can interact strongly with the electric fields of photons (Smith and Dent, 2005). This interaction is caused by the excitation of the surface plasmon by an excitation laser source which greatly increases the local electric field experienced by the adsorbed target molecule (Campion and Kambhampati, 1998). As this interaction is dependent upon the degree the surface plasmon can be excited by the laser it is strongly dependent on the wavelength and consequently the degree of signal enhancement is also wavelength dependent. Thus, matching the excitation laser wavelength to the localised surface plasmon resonance frequency of the metal surface or nanoparticle (NP) needs to be considered when performing SERS experiments.

Conventionally, SERS enhancement is produced when the metal NP plasmon resonance wavelength is as close as possible to the wavelength of the excitation laser (Yong-Hyok et al., 2012). However, it has been shown that maximum enhancement is possible when the excitation laser wavelength is blue shifted in respect to the localised surface plasmon resonance of the metal NP, up to one-half of the vibrational frequency (Kosuda et al., 2010; McFarland et al., 2005). This phenomenon explains the signal enhancement that is produced even when the laser wavelength is "off-resonance" with respect to the localised surface plasmon resonance frequency of the metal NP. This leads to the potential for designing SERS sensors that are not limited by having to match resonance frequencies of both the metal surface and excitation laser (Sivapalan et al., 2013).

Another theory of SERS enhancement is the so-called chemical enhancement, or charge transfer, mechanism. First proposed in 1979 by Gersten, Birke, and Lombardi (Gersten et al., 1979) the charge transfer theory suggests that the chemical bonding of the target analyte to the metal surface and the subsequent mixing of analyte-metal energy levels results in an enhancement in Raman signal similar to resonance Raman effects (Gersten et al., 1979). These effects are mainly manipulated by changes in electrode voltage (NB voltage only can only be applied if metal electrodes are used as the SERS-active surface), or by excitation laser energy, or a combination of the two (Lombardi et al., 1984). This process is complicated by the fact that some experiments have shown a positive relationship between excitation energy and resonance voltage (Macomber and Furtak, 1983) whilst others have shown a negative relationship between the two factors (Furtak and Roy, 1983; Lombardi et al., 1984).

While there has been an abundance of modern-day studies demonstrating that SERS enhancement mechanisms are primarily attributable to either electromagnetic theory or charge transfer theory, there is still a matter of great debate as to what degree each is responsible for the final result (Birke et al., 2016; Etchegoin and Le Ru, 2010; Smith and Dent, 2005). This is because neither theory can fully explain the SERS phenomena. While charge transfer theory does adequately explain the
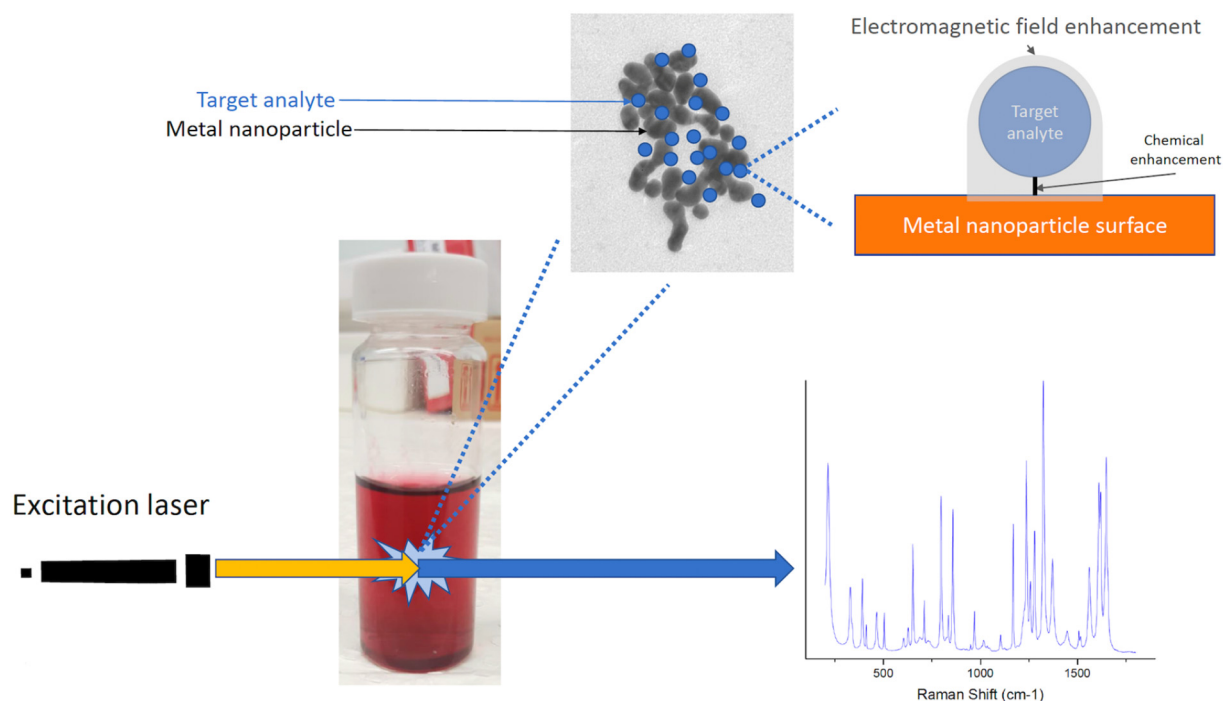

Fig. 1. Overview of SERS enhancement.

interaction and resulting signal boost between the analyte and metal surface by this definition the signal boost must be a result of only the first layer of the analyte adsorbing onto the metal surface. In reality the signal boost may be a result of the field enhancement occurring from a subsequent layer of interaction - which is a phenomena explained by electromagnetic theory. Different levels of SERS signal enhancement have been reported for samples of multi-layered metal NPs (Liu et al., 2016), an observation which is not adequately explained by charge transfer theory which does not account for any enhancement in signal gained away from the surface (Smith and Dent, 2005) (Lombardi and Birke, 2008). Conversely, charge transfer theory can explain certain aspects of SERS phenomena that electromagnetic theory cannot, and so a combination of both is now thought to be responsible for the process. While the details of SERS mechanisms are still being explored by many researchers, an understanding of the electromagnetic and charge transfer mechanisms provides sufficient understanding for the design and optimization of SERS substrates and experiments.

For SERS experiments that utilise colloidal nanoparticles, the type, shape and surface treatment of metals used must be taken into consideration. Gold and silver are the two most common metals to use for SERS substrate creation because of their optical properties (Etchegoin and Le Ru, 2010). Briefly, the fact that these metals are able to produce surface plasmon resonance as a result of their dielectric functions being both high in magnitude and negative, enables them to produce a localised surface plasmon resonance (Etchegoin and Le Ru, 2010; Kosuda et al., 2010). This contributes greatly to the local electromagnetic field enhancement when the metal is excited by photons. Among the wide variety of available SERS substrates, citrate-reduced silver colloids (Lee and Meisel, 1982), hydroxylamine-reduced silver colloids (Leopold and Lendl, 2003), and borohydride-reduced gold colloids (Frens, 1973) are among the most widely used due to their relatively low cost and the ease of preparation, as well as the possibilty to tune their performance by varying the size of the final nanoparticle.

Particle size is important as it has a direct effect on both Raman signal enhancement and the stability of the substrate (Etchegoin and Le Ru, 2010). Because of the difficulty in creating completely uniform NPs, which can lead to unpredictable NP behaviour, inconsistencies in SERS responses are a common problem. The myriad of viable combinations of NP size, shape, and uniformity makes optimisation of the experimental setup to find the conditions that produce the highest degree of enhancement while still being reliable, very difficult.

It may be evident to the reader at this stage that the enhancement factor in SERS greatly depends on the precise set-up of the experiment. This primarily affects the detection limit rather than reproducibility. Error margins are not generally affected as it is quick and easy to take multiple readings and average the signal. The presence of multiple target substances can be addressed by the use of library spectra from certified reference standards to identify the peaks of interest. The use of specific and selective linker molecules between the nanoparticle and target compounds to act as a filter to pick specific compounds from the many that may be found in the environment is also possible (Weerathunge et al., 2014). At present, as this is such a new field, there are no guidelines for choosing the "best" protocol and an environmental scientist working in this area can expect to conduct a number of optimisation steps before settling on a method suitable for their particular question.

Computational approaches may be able to help to resolve this challenge. Levene et al. [30] designed a multi-objective evolutionary algorithm (MOEA) to obtain optimal experimental conditions with the minimum number of experiments, saving time and resources compared to a traditional exhaustive empirical experimental approach. The authors successfully determined the optimal SERS conditions for detection of propranolol with multiple variables (excitation wavelength, SERS colloid type, colloid aggregation agents, NP concentration) with only ~4% of the number of experiments necessary compared to an empirical approach (315 vs 7785 experiments) while obtaining a limit of detection

25 times lower than in previous studies on the same compound (Levene et al., 2012). It should be noted that for each target analyte there will be a different optimal SERS experimental setup, due to the analyte-specific nature of SERS interactions. The aforementioned MOEA is not the sole "best practice" optimisation protocol, this will differ depending on the experimental aims of each individual researcher for their respective projects (Fisk et al., 2016).

2.2.1. SERS substrate aggregation and signal enhancement

SERS active nanoparticles are known to form aggregates and these aggregates can and do increase in size over time. This process can increase signal intensity at higher excitation frequencies (Faulds et al., 2004) however, the effects of aggregation are not uniform, and have been shown to reduce signal intensity at certain excitation frequencies, resulting in poor reproducibility of results for NPs that are continuously aggregating over the course of measurements (Xiong and Ye, 2014). The design of NP-based SERS experiments for analyte detection and quantification typically require identifying the experimental conditions and timeframe for which NP interactions are strong enough to provide the plasmon resonances required to generate the SERS response but before further aggregation decreases signal reproducibility. Sonication of the NPs to dissociate aggregated clusters can recover the individual NPs and acceptable SERS performance if needed (Yanilkin et al., 2015).

Controlled aggregation of SERS NPs can be used to greatly enhance signal strength. SERS signal boosts as high as 10^{14} have been reported in specific conditions (Xu and Käll, 2002) (Xu and Käll, 2006). This is usally very difficult to achieve and only occurs under ideal circumstances as it requires the NPs to be brought very close together in a very controlled way (Moskovits, 2005). Increases of signal strength of around tenfold, while much lower, are relatively easily achievable and increases beyond that are possible if the necessary time is spent on experimental optimisation.

SERS is unique among spectroscopy techniques in that there is immense potential for extremely low limits of detection through fine tuning of the experimental approach (Pieczonka et al., 2010). As mentioned above, single molecule detection has been reported (Pieczonka and Aroca, 2008). The experimental conditions required for ultra-low or single molecule detection are however, difficult to attain due to three main limitations: i) poor control of colloidal interactions ii) significant uncertainties regarding the actual number of molecules in the studied volume, and iii) poor statistics for identifying single molecule SERS events - as only molecules bound to a site of significant signal enhancement produce detectable signals (Etchegoin and Le Ru, 2008). Some of the strategies employed to overcome these difficulties include Langmuir-Blodgett films, which provide a significantly better estimate of the concentration of molecules bound to the SERS substrate and thus a stronger proof of single molecule detection (Pieczonka and Aroca, 2008); Tip Enhanced Raman scattering, which features extremely high degrees of control of a single substrate hotspot producing a signal (Pettinger et al., 2002); and bi-analyte SERS, which works as a contrast method, isolating single molecule signals of one analyte in the background signal of another, enabling measurements at higher concentrations while maintaining the possibility of single molecule detection (Le Ru et al., 2006).

One might ask why use NPs at all, why not a continuous substrate? It is of course possible to do this but the signal enhancement is not as strong as with nanoparticles. This is because with a surface the plasmon enhancement only comes from one direction (from the surface) whereas with nanoparticles it is possible to trap the compound(s) of interest between two (or more) particles and thus receive a combined signal enhancement from each.

Single molecule detection of pollutants in environmental samples is likely to be impossible, at least in the foreseeable future, due to interference from the sample matrix and the diversity of compounds present in a single sample. However, for many applications single molecule detection is not required. SERS has the potential to be of broad use for low

concentration detection of a variety of compounds from various classes of interest such as heavy metals, pesticides, pharmaceuticals, endocrine disruptors and perfluorinated compounds. A brief overview of SERS detection of compounds in each of these classes is given below. A discussion of the pros and cons of such detection methods for each class is then provided in the discussion.

3. Use of SERS in detecting pollutants

3.1. Heavy metals

Heavy metals are potentially toxic elements that are almost ubiquitous in the environment, mainly as a product of industrialization. Mercury is one of the most toxic heavy metal pollutants with bioaccumulation of the organic form of this compound resulting in severe neurological damage and other effects in humans (Clarkson, 2002). This makes mercury a prime analyte of interest for environmental monitoring studies. Conventional approaches for detecting mercury are inductively coupled plasma mass spectrometry (ICP-MS), electrochemical methods, cold vapour atomic absorbtion spectroscopy and liquid chromatography (Kandjani et al., 2015). However, these techniques have the disadvantage of requiring extensive sample preparation, highly specialized and expensive equipment and related training of personnel, and long sample measurement times. This is also true for other ubiquitous heavy metal pollutants such as chromium. In addition, conventional methods are often unable to identify between different oxidation states of metals (Kandjani et al., 2015).

SERS is a promising method for the detection of heavy metals but is not without issues. Both mercury and silver form monoatomic ions which is a problem for SERS detection due to the fact that their small scattering cross sections usually do not generate Raman spectra (Li et al., 2013). Several workers have used functionalized NPs to get around this. Such methods range from simpler approaches such as modifying gold nanorods with thymine (with the limit of detection being 1 μg/L (Yang et al., 2017a)), to more complex methods such as placing Ag NPs in a magnetic cobalt ferrite ($CoFe_2O_4$) frame combined with single-stranded DNA and single walled carbon nanotubes on the NP surface. This latter approach gave a detection limit of 0.84 picomoles (or ~0.00016 μg/L) (Yang et al., 2017b). Similarly, Chen et al. devised a 4-mercaptopyridine (4-MPY)-modified Ag NP system that can achieve detection levels of Hg^{2+} of 6.14 μg/L in laboratory water when in the presence of spermine (Chen et al., 2014). The spermine was used to cause a controlled aggregation of the Ag NPs, resulting in an increase in signal. Utilisation of synthetic ZnO nanoarrays plated with Ag NPs has also been proven to be a viable SERS platform for detecting Hg^{2+} at a limit of approximately 0.45 μg/L, with the added benefit of being capable of

100% recovery, to both eliminate Ag NP pollution and to be able to reuse the material for subsequent sensing operations (Kandjani et al., 2015).

As SERS revolves around using functionalized NP the rise of SERS as an analytical technique means one environmental aspect to consider is NP pollution in the environment. Using a filtration technique combined with SERS, Guo et al. were able to rapidly monitor Ag NPs in real environmental water at a limit of 5 μg/L, which is 20 times lower than conventional centrifugation methods (Guo et al., 2016b). The same workers have also more recently examined the properties of ferbam and compared its binding affinities and suitability to 6 other sensor molecules for the detection of AgNPs without a filter and found that ferbam provided the best detection limits, 0.1 mg/L for surface water and 0.57 mg/L in spinach juice (Guo et al., 2016a).

A list of metals analysed with SERS along with reported detection limits is given in Table 1.

3.2. Pharmaceuticals

Pharmaceuticals are now an integral feature of everyday life in societies with a functioning healthcare system. The direct effects of pharmaceuticals in the environment on human health are not well known but the environmental concentration of these pollutants are often thought of as too low of a concentration to have any significant effect. However, there are complicating factors that should be considered such as the life stage of an organism (e.g. adult vs child) (Spurgeon et al., 2010). The effects of exposure to low doses of a complex mixtures of pharmaceutical compounds are also generally not taken into account in environmental risk assessment of such compounds (Jones et al., 2004). A list of pharmaceuticals analysed with SERS along with reported detection limits is given in Table 2.

Raman Spectroscopy and SERS are commonly used to detect pharmaceuticals in biological samples, such as human blood, saliva, or urine, often in the context of illicit drug detection. The difficulty in using a spectroscopic technique to analyse aqueous biological analytes, compared to analytes suspended in solvent, is that there are a myriad of highly scattering interfering non-target compounds present in the sample, as well as random introduced noise, which affect measurement reproducibility. Wróbel et al. solved this problem by using a Raman excitation wavelength red-shifted to 830 nm, this both reduces fluorescence interference and avoids the absorption peaks of non-target compounds, such as haemoglobin (Wróbel et al., 2017). To obtain SERS enhancement in this case, silver NPs encased in a gold shell were used. With this approach the authors successfully manage to detect addictive barbiturate α-hydroxyalprazolam at a limit of detection of

Table 1
Tabulated literature results for SERS detection of heavy metals.

SERS substrate characteristics	Targeted analyte	Excitation wavelength	Integration time	Sensitivity	Sample medium	Ref.
Silver NPs deposited onto Zinc Oxide nanoarray	Hg^{2+}	785 nm	5 s	0.4 μg/L	SERS substrate	(Kandjani et al., 2015)
Conjugation of ferbam to aggregated Ag NPs via incubation, then centrifugation	Ag NP	780 nm	2 s	0.1 μg/L	Dried precipitate on Au slide	(Guo et al., 2016b)
Conjugation of ferbam to aggregated Ag NPs via filtration through single membrane	Ag NP	780 nm	2 s	5 μg/L	Filtration membrane	(Guo et al., 2016b)
Thymine-adsorbed Au Nanorods	Hg^{2+}	632.8 nm	10 s	20 ng/L	Pure water	(Yang et al., 2017a)
Thymine-adsorbed Au Nanorods	Hg^{2+}	632.8 nm	10 s	1 μg/L	River water	(Yang et al., 2017a)
Ag NPs in $CoFe_2O_4$ shell modified with single-stranded DNA and single-walled carbon nanotubes on NP surface	Hg^{2+}	532 nm	10 s	16.9 μg/L	River water	(Yang et al., 2017b)
4-MPY-modified hydroxylamine Ag NPs incubated with spermine	Hg^{2+}	632.8 nm	4 s	6.1 μg/L	Deionised water	(Chen et al., 2014)
Conjugation of ferbam to aggregated Ag NPs via incubation, then centrifugation	Ag NP	780 nm	2 s	0.1 μg/L	Pond water dried on Au slide	(Guo et al., 2016a)
Conjugation of ferbam to aggregated Ag NPs via incubation, then centrifugation	Ag NP	780 nm	2 s	0.5 μg/L	Spinach juice dried on Au slide	(Guo et al., 2016a)

Table 2
Tabulated literature results for SERS detection of pharmaceuticals.

SERS substrate characteristics	Targeted analyte	Excitation wavelength	Integration time	Sensitivity[a]	Sample medium	Ref.
Silver-core gold-shell spheroidal NPs	α-Hydroxyalprazolam	830 nm	5 s	0.33 μg/L	Human blood	(Wróbel et al., 2017)
Citrate-reduced gold NPs	Propanolol	785 nm	23 s	2.36 μg/L	Solution	(Levene et al., 2012)
Citrate-reduced silver NPs	Mephedrone	633 nm	20 s	1.60 μg/L	Solution	(Mabbott et al., 2013)
Chitosan-reduced gold NP film	Paracetamol	633 nm	10 s	151.16 μg/L	Dried on SERS substrate	(Santos et al., 2014)
Magnetron-sputtered silver nanorod chips	Methamphetamine + amphetamine	785 nm	10 s	50 μg/L	Dried urine on SERS substrate	(Nuntawong et al., 2017)

[a] Original values in uM/pM. Units converted here to parts-per notation for easy comparison between experiments.

0.3 mg/L, notably using only a portable Raman spectrometer and with an integration time of just 5 s.

Levene et al. performed an exhaustive study on optimising SERS detection of the beta-blocker propranolol using MOEA (as described in the "SERS" section above) (Levene et al., 2012). Aside from optimising the amount of time and resources needed to reach optimal sensing parameters, they successfully lowered the limit of detection to 2.36 μg/L, which is a 25-fold decrease compared to previously published studies for the same compound using unoptimized SERS methods. The robustness of the process means that it can be reasonably expected to be able to be applied for environmental samples.

Mabbott et al. used a fractional factorial design to reduce the number of experiments needed to optimise SERS detection of the illicit drug mephedrone (Mabbott et al., 2013). They achieved a limit of detection of 1.60 mg/L using a portable Raman spectrometer, again demonstrates that this optimised approach is potentially suitable for in-field environmental detection.

Santos et al. demonstrated the viability of a chitosan-reduced gold NP substrate for the environmental detection of paracetamol, one of the most ubiquitous pharmaceuticals in the world (Santos et al., 2014). However, it is difficult to determine how effective a sensing platform their substrate was as the authors did not publish empirical data or a limit of detection for their study. The concentration of analyte that they successfully detected in their study was 10 mM, or approximately 151 μg/L. This will be insufficient for environmental detection, as the predicted environmental concentration of paracetamol is around 10 μg/L or lower (Ong et al., 2018). The experimental method would also be improved if the aim is to use it in real-world conditions, as the authors chose to fix the paracetamol solution onto the SERS substrate film via drop deposition and air drying before analysis via a benchtop Raman spectrometer. This is suboptimal for reproducibility purposes, as uncontrolled air drying of the sample tends to produce an uncontrollably heterogenous analyte surface. This results in SERS spectra that are difficult to replicate and demonstrates site-to-site variability. This is because the SERS spectral response will be different based on the orientation of each paracetamol molecule as it is adsorbed onto the NP surface. This approach may also lead to the deposition of matrices of pure paracetamol layered on top of the substrate which may interfere with SERS responses.

Nuntawong et al. (2017) utilised an in-house fabricated SERS chip made from uniformly spaced and shaped silver nanorods as the substrate to deposit urine samples on in order to detect methamphetamine, and its primary metabolite, amphetamine. Initially, the impurities in the urine samples obscured the SERS reaction of the target analytes. The authors solved this problem by acidifying the sample using nitric acid, which transformed urea into urea nitrate which then precipitated out of solution. The remaining urea content was then positively ionised and so lost the ability to bind to the silver nanorod surface. In this way the researchers increased the reliability and reproducibility of their results by preventing sample impurities obscuring the spectral response, while maintaining a high degree of sensitivity and a fast measurement. It was also possible to detect multiple diagnostic bands to determine the presence of methamphetamine and amphetamine. This would likely be useful when discerning the urine of a methamphetamine user from a user of amphetamine-type stimulants, and the method could be adapted to other, non-medical applications where impurities could be removed via precipitation (or similar methods) such as testing of wastewater for drug residues.

3.3. Endocrine disrupting compounds

Endocrine disrupting compounds (EDCs) are one of the most ubiquitous classes of aquatic pollutants and have received much attention since the discovery of their environmental effects in the 1980s (Jobling et al., 1998). Estrogens are known to be ubiquitous in the environment and have been shown to bio-accumulate in animals and humans with a subsequent possible interference with the endocrine system, thus posing as a significant health threat if unmanaged (Rahman et al., 2009).

Recent literature on EDC detection utilising SERS is summarised in Table 3. This area of work has mainly focused on the detection of a particular estrogen, 17ß-estradiol, which is naturally synthesised in the body and artificially synthesised for various medical treatments. Detection of such compounds in the environment is generally in the ng/L range or lower (Liu et al., 2018). Currently, LC-MS is the main method employed to reliably detect 17ß-estradiol at such concentrations but SERS does have the potential to detect compounds at these levels.

Liu et al. utilised SERS to detect 17ß-estradiol in both lab and environmental samples (river water), attaining a detection limit of 0.05 pM and 1.3 pM respectively (Liu et al., 2018). Their SERS system comprised Au NPs in an Ag shell, labelled with 4-mercaptobenzoic acid (4-MBA) and an aptamer (oligonucleotide or peptide that bind to a specific target molecule) specific to 17ß-estradiol, granting the system high degrees of sensitivity as well as selectivity. This study was the first to utilise aptamers with SERS for selective detection of 17ß-estradiol. Since that time aptamers in conjunction with NPs have been implemented as a selective detection method, due to the high binding affinity of the target analyte and designed aptamer (Sefah et al., 2009). This approach has been popular in the biomedical field due relative ease of developing precise aptamers. Such applications has commonly been coupled with complimentary detection techniques to SERS, such as colorimetric detection (Li et al., 2015). It must also be kept in mind that the cost of developing a new aptamer from scratch (as opposed to purchasing an existing one) can run into tens of thousands of dollars.

Current SERS literature on EDC detection has mostly been in clinical contexts, not environmental. Rosner et al. recognised a demand for a sensing technique for 17ß-estradiol capable of routine sensitive detection at concentrations in the ng/L range, which is the predicted concentration in tissue at which 17ß-estradiol can have a significant effect (Rosner et al., 2013). Wang et al. devised a SERS-based assay for detection of 17ß-estradiol in human serum, achieving a limit of detection of 0.65 pg/mL (Wang et al., 2016). Although this limit does not meet the demands set by Rosner et al., the method used does exceed the measurement speed, sensitivity, and practicality of conventional methods (HPLC-MS, radioimmunoassay, enzyme-linked immunoabsorbent assay) (Wang et al., 2016). Their SERS system is immune-complexometric where 17ß-estradiol is conjugated onto Au NPs via a PEG spacer, then separation from the analyte solution using magnetic

Table 3
Tabulated literature results for SERS detection of hormones and endocrine disrupting compounds.

SERS substrate characteristics	Targeted analyte	Excitation wavelength	Integration time	Sensitivity[a]	Sample medium	Ref.
Au@Ag core shell NP labelled with 4-MBA and 17ß-estradiol aptamer	17ß-estradiol	532 nm	5 s	13.62 ng/L	Distilled water	(Liu et al., 2018)
Au@Ag core shell NP labelled with 4-MBA and 17ß-estradiol aptamer	17ß-estradiol	532 nm	5 s	0.35 µg/L	Filtered river water	(Liu et al., 2018)
Au NPs labelled with MGITC and 17ß-estradiol-specific nanotags conjugated to magnetic beads with anti-17ß-estradiol antibodies	17ß-estradiol	632.8 nm	1 s	0.65 ng/L	Human serum	(Wang et al., 2016)

[a] Original values in uM/pM. Units converted here to parts-per notation for easy comparison between experiments.

beads with anti-17ß-estradiol antibody as the separation agent into a capillary tube prior to measurement. They compared this SERS method to a chemiluminescence immunoassay (ARCHITECT) to assess the clinical reliability of SERS and found that the limit of quantification of SERS was 5 times lower compared to ARCHITECT (4.8 pg/mL vs 25.0 pg/mL, respectively), thus showing that SERS-based immunoassays can potentially be used for rapid screening in clinical applications and perhaps also environmental ones.

3.4. Perfluorinated compounds

An emerging environmental contaminant of high concern, perfluorinated compounds (PFCs) are synthetic organic hydrocarbon compounds where the hydrogens in the alkyl chain are replaced by fluorine atoms. Manufactured for over 50 years and designed to be extremely stable perfluorinated compounds have found ubiquitous use in modern society, such as in firefighting foams, water-resistant clothing, and cooking utensils (Stahl et al., 2011). It is because of this usefulness in society and the inherent strength of its carbon-fluorine backbone that that perfluorinated compounds persist in the environment and likely bioaccumulate (Stahl et al., 2011).

Although the Raman band assignments for several common PFCs have been published (Amorim da Costa and Santos, 1983), these have only been reported using conventional Raman Spectroscopy not SERS. Furthermore, this publication is almost 40 years old and does not cover all common, modern perfluorinated compounds, such as perfluorooctanesulfonic acid (PFOS). However, the unique and abundant carbon-fluorine bonds generate a number of distinct fingerprint Raman bands denoting the presence of a perfluorinated compound, such as the CF_3 band (725–782 cm^{-1}), CF_2 band (691 cm^{-1}), and aromatic CF band (569–589 cm^{-1}) that will likely still be useful for future SERS detection studies of this group.

In the contemporary literature there is a noticeable lack of SERS studies performed to detect PFCs at environmentally relevant concentrations but those available are summarised in Table 4. Fang et al. utilised a dual-substrate comprised of Ag NPs on a surface of graphene oxide to successfully detect pentadecafluorooctanoic acid (PFOA) ion-pared to a Raman dye (both Ethyl Violet and Methylene Blue were used) at a limit of 50 µg/L (Fang et al., 2016). However, to achieve this, the authors had to ion-pair the PFOA sample to a Raman active dye (that could greatly enhance the signal) rather than directly adsorbing PFOA to the SERS substrate. Because of the large signal of the dye obscuring the PFOA signal, they used the dye signal rather than the PFOA signal for quantification, meaning the results are ambiguous.

In the future it may prove possible to detect PFOA with SERS without relying on a dye. It is feasible for example to use nanoparticle-based optical sensors for selected anionic contaminants (such as many PFCs) with potential for environmental sensing. Fang et al. suggested the use of Au NP-based sensors for detecting fluoride ions for example (Fang et al., 2017). They acknowledged that a significant challenge in their context of individual anion detection, would be from other co-existing anions interfering with the detection and may even result in false positives because handheld Raman spectrometers are not yet as sophisticated as benchtop instruments in terms of selectivity and sensitivity. However, there are potential solutions to these challenges, such as modifying Au NPs to enable selective binding of a target analyte to the Au NP surface using thiol chemistry (Niu et al., 2014), or using thiol-attached aptamers conjugated to Au NPs (Menaa et al., 2011). False positive detection results can be reduced with a combination of statistical techniques enabling a more accurate measurement of important analytes (Chuong et al., 2017).

3.5. Pesticides

Pesticides comprise of substances that are designed to destroy or repel pests. They are commonly used to prevent spoilage of crops and have become indispensable in modern agriculture (Pretty, 2008). Modern pesticide usage is extensive, often resulting in indiscriminate exposure of the pesticide to non-targeted organisms.

In terms of mobility pesticides are water soluble and often deployed as an aerosol, resulting in both liquid and gaseous phase pollution. Pesticides tend to persist in ecosystems, bioaccumulating and eventually affecting humans (Stanley and Preetha, 2016). Fish can also be acutely poisoned outright by pesticide exposure, with most common pesticides having a low LC_{50} value, often in the µg/L to mg/L range. In this way pesticides have a significant environmental impact. Fortunately, pesticides as analytes for Raman spectroscopy-based detection studies are common in the literature and these are summarised in Table 5. With the advent of portable Raman spectrometers enabling rapid in-situ screening of samples, a new wave of studies are being performed worldwide focusing on detecting these pollutants on the surface of crops.

SERS is also very relevant in this context, as portable Raman instruments often do not have the analytical sensitivity of a benchtop instrument, nor are field conditions as optimal as a laboratory setting for analysis. When considering SERS substrates for portable instrument usage, simple solutions that can be replicated reliably and provide good analyte sensitivity are generally favoured.

Table 4
Tabulated literature results for SERS detection of PFCs.

SERS substrate characteristics	Targeted analyte	Excitation wavelength	Integration time	Sensitivity[a]	Sample medium	Ref.
Ag nanospheres on graphene oxide surface membrane with ethyl violet dye	ethyl violet (ion paired to PFOA)	532 nm	5 s	50 µg/L	Graphene oxide-coated silicon surface	(Fang et al., 2016)
Ag nanospheres with ethyl violet dye	PFOA	532 nm	5 s	500 µg/L	Silicon surface	(Fang et al., 2016)

[a] Original values in uM/pM. Units converted here to parts-per notation for easy comparison between experiments.

Table 5
Tabulated literature results of SERS detection of pesticides.

SERS substrate characteristics	Targeted analyte	Excitation wavelength	Integration time	Sensitivity[a]	Sample medium	Ref.
Citrate-reduced AuNP immobilised onto UF membrane	Thiabendazole	785 nm	1 s	1 mg/L[b]	Solution	(Hong et al., 2017)
Citrate-reduced AuNP immobilised onto UF membrane	Thiabendazole	785 nm	1 s	125 μg/L[b]	Solution	(Hong et al., 2017)
Citrate-reduced AuNP	Various pesticides[c]	780 nm	2 s	0.25 mg/L to 0.5 mg/L	Tea leaf	(Hou et al., 2015)
Citrate-reduced AuNP	Various pesticides[c]	780 nm	2 s	0.01 mg/L to 0.02 mg/L	Apple peel	(Hou et al., 2015)
Laser-annealed Au films / PLD-deposited 3D Au nanostructures in air / Laser-ablated AuNP	DDT	785 nm	10 s	340 mg/L[d]	Solution on silicon	(Nedyalkov et al., 2017)
Laser-annealed Au films / PLD-deposited 3D Au nanostructures in air / Laser-ablated AuNP	Ammonium nitrate	785 nm	10 s	50 mg/L[d]	Solution on silicon	(Nedyalkov et al., 2017)
Hybrid Au nanorod and Azo AuNP assembly	NO_2^- ions	785 nm	20 s	36.8 μg/L[b]	Silicon wafer	(Li et al., 2018)
Citrate-reduced AuNP	Phosmet	780 nm	2 s	0.5 mg/L	Silicon wafer	(Luo et al., 2016)
Citrate-reduced AuNP	Thiabendazole	780 nm	2 s	0.1 mg/L	Silicon wafer	(Luo et al., 2016)

[a] Original values in uM/pM. Units converted here to parts-per notation for easy comparison between experiments.
[b] Data obtained using portable Raman spectrometer.
[c] Pesticides studied include isocarbophos, phorate, imidacloprid, detlamethrin.
[d] Value given is not LOD; authors did not carry out an LOD study, focus was on comparing signal quality between 3 different variations of SERS substrate.

Hong et al. fabricated a simple SERS sensor for use with a portable Raman spectrometer which comprises of citrate-reduced spherical gold nanospheres physically immobilised onto an ultrafiltration membrane via vacuum suction (Hong et al., 2017). They also immobilised their target analyte, thiabendazole, onto the SERS substrate using the same method, notably concentrating up the analyte and ensuring binding to the Au NPs simultaneously. They performed this measurement on thiabendazole standards and on thiabendazole extracted from the surface of orange peel achieving an LOD of 125 μg/L. Similarly, Hou et al. used a hybrid method using SERS where they drop citrate-reduced Au NPs directly onto the surface of a plucked tea leaf and performed a measurement on the leaf itself using a benchtop Raman spectrometer (Hou et al., 2015). In this way, the authors presented a compromise between using a more sensitive benchtop instrument, and the convenience and rapid screening of in-situ measurements.

One of the difficulties in pesticide detection is in selecting which pesticides to study. There are thousands of pesticides in modern agricultural usage, so constructing highly specific aptamers for each would be a costly exercise. One of the ways to combat this is to create a SERS sensor targeting a component that is common across multiple pesticides. Li et al. have developed a SERS sensor for the detection of nitrite, which is found in meat preservatives and associated with nitrite-containing pesticides (Li et al., 2018). Sample preparation was simplistic, requiring only the liquid-phase analyte to be mixed with the gold NP solution for 5 min before being dried upon a silicon wafer prior to detection via a portable Raman spectrometer, all performed in ambient conditions. This method is well suited for routine environmental sensing and the degree of sensitivity is also encouraging A limit of detection of 37 μg/L was obtained in this work (Li et al., 2018). This is well below the WHO recommendation of maximum nitrate ion concentration in drinking water (50 mg/L, or 50 mg/L) (Ward et al., 2018). Notably, the method detection limit of nitrite cited by the WHO via Ion Chromatography (9 μg/L) is within 1 order of magnitude of the limit of detection achieved via in-situ SERS with a total of 5 min and 20 s for sample preparation and measurement time (37 μg/L) (Ward et al., 2018). This further demonstrates the potential for SERS as a method for environmental detection of pollutants.

4. Preparative techniques for SERS

When considering the future evolution of SERS applications for environmental pollutant detection, a desirable method is one that can be performed in the field with a low time, manpower, and expertise costs, that enables specific detection of a target analyte, and is reproducible. One such approach is to use Thin Layer Chromatography (TLC), a chromatographic technique used to separate non-volatile mixtures, to achieve sample separation, followed by SERS analysis for sample measurements. Thin-layer chromatography is performed on a sheet of glass, plastic, or aluminium foil, which is coated with a thin layer of adsorbent material, usually silica gel, aluminium oxide (alumina), or cellulose. The sample can then easily be transported for further analysis. This combination of chromatography and spectroscopy both enables clear distinction between analyte types based on mass, concentrating the sample for ease of measurement, and being a viable method to perform in the field, which opens up potential for in-situ real time water quality monitoring. Usage of TLC-SERS to detect analytes at extremely low concentrations was first published in 1982 by Séquaris and Koglin when they used Silver NPs on a TLC silica gel plate to detect 9-Methylguanine (Séquaris and Koglin, 1982). Since then, the technique has been demonstrated to be able to be of use in SERS based environmental analysis (including for pesticides) and the results are summarised in Table 6.

Li et al. used TLC-SERS to detect aromatic pollutants in real wastewater samples, reporting detection of p-toluidine, p-nitroaniline, and lentine at concentrations of 91 mg/L, 173 mg/L, and 274 mg/L, respectively (Li et al., 2011). Their method comprised of regular TLC separation of wastewater samples, followed by drop-deposition of Ag NPs onto each separated spot, followed by SERS measurements using a portable Raman spectrometer with Raman probe. To assess the viability of their results, they then used GC–MS to analyse the same samples and compared the detected concentrations of the 3 mentioned compounds. The variation between the measured concentration was found to be <15% between the two techniques, but the measurement time was 16.8 times faster with Raman compared to GC–MS (50 s vs 14 min, respectively). The limit of detection for TLC-SERS for lab samples was between 8 μg/L and 0.2 mg/L for their range of target pollutants.

Lv et al. used a TLC-SERS method for detecting ephedrine in dietary slimming products and were able to reach a detection limit of 0.01 mg/L (Lv et al., 2015).

Yao et al. took a similar approach for the on-site detection of organophosphate pesticide methidathion in tea leaves and compared TLC-SERS detection with GC–MS (Yao et al., 2013). TLC-SERS detection limits of spiked tea leaf samples for methidathion were within 15% deviation compared to GC–MS detection of the same samples. The authors compared the viability between citrate-reduced Au NPs and citrate-reduced Ag NPs and found that Ag NPs provided the best signal enhancement, likely due to the fact that Ag NPs inherently produce a stronger SERS enhancement (Yao et al., 2013). It a slighty, surprising

Table 6
Tabulated literature results of TLC-SERS detection of environmental pollutants.

SERS substrate characteristics	Target analyte	Excitation wavelength	Integration time	Sensitivity[a]	Sample medium	Ref.
Ag NPs drop-cast onto Si60 - F$_{254}$ TLC plate	Various aromatic compounds[c]	785 nm	50 s	5 µg/L – 0.2 mg/L[b] (5 µg/L – 0.2 mg/L)	Solution	(Li et al., 2011)
Ag NPs drop-cast onto Si60 - F$_{254}$ TLC plate	p-toluidine	785 nm	50 s	91 mg/L[b] (91 mg/L)	Wastewater	(Li et al., 2011)
Ag NPs drop-cast onto Si60 - F$_{254}$ TLC plate	p-nitroaniline	785 nm	50 s	173 mg/L[b] (173 mg/L)	Wastewater	(Li et al., 2011)
Ag NPs drop-cast onto Si60 - F$_{254}$ TLC plate	Lentine	785 nm	50 s	274 mg/L[b] (274 mg/L)	Wastewater	(Li et al., 2011)
Ag NPs drop-cast onto Si80 - GF$_{254}$ TLC plate	Methidathion	785 nm	0.8 s	0.1 mg/L[b] (0.1 mg/L)	Solution	(Yao et al., 2013)
Ag NPs drop-cast onto Si80 - GF$_{254}$ TLC plate	Methidathion	785 nm	0.8 s	4.87 mg/L[b] (4.87 mg/L)	Tea extract	(Yao et al., 2013)
Ag NPs drop-cast onto Si60 - F$_{254}$ TLC plate	Ephedrine-based compounds	785 nm	5 s	0.01 mg/L[b] (0.01 mg/L)	Dietary supplement	(Lv et al., 2015)

[a] Some original values in uM/pM. Units converted here for easy comparison.
[b] Data obtained using portable Raman spectrometer.
[c] Compounds for which LODs were established: aniline (0.1 mg/L), benzidine (8 µg/L), chlorobenzene (0.2 mg/L), and pyrocathechol (0.05 mg/L).

result for 785 nm excitation and the structure of methidathion suggests that it should interact strongly with a Au surface.

5. Discussion

Raman Spectroscopy boasts much higher efficiency than mass spectrometry (MS) in terms of sample pre-processing and measurement runtime. Furthermore, measurements can be obtained quite literally in the field which is not generally possible with mass spectrometry. Crucially, when combined with Surfaced Enhancement techniques, Raman Spectroscopy can potentially match mass spectrometry in terms of sensitivity. While at present the sensitivity is not at the required levels for routine detection of environmental pollutants the bulk of the SERS literature on environmental pollutant detection published in recent years has showcased how the field is slowly moving towards this aim and is already matching the detection limits achieved in the early days of mass spectrometry. A flow chart illustration of a possible workflow for SERS experiments is given in Fig. 2.

Going forward it is likely that detailed experimental protocols will be needed for SERS analysis of the environment. The wider availability of verified library spectra of common pollutants and associated software solutions to enable fast and simple comparison is also needed to help deal with mixtures - as has been the case for mixture analysis via Nuclear Magnetic Resonance Spectroscopy (e.g. the Chenomx NMR Suite software - https://www.chenomx.com/).

In terms of NPs, gold can be considered as a more suitable material for SERS than silver, particularly in the context of real-time environmental monitoring, because of their specific properties. Gold NPs have a higher stability and thus longer SERS lifetime than silver NPs, are excellent fluorescence quenchers, will not dissolve in river water and are not as environmentally hazardous as silver NPs. Furthermore, most modern portable Raman spectrometers utilise a 785 nm excitation laser, which is more appropriate for gold rather than silver NPs rather due to gold NPs exhibiting surface plasmon resonance, and subsequently higher SERS signal enhancements, at 785 nm laser excitation.

For heavy metal pollutants, much of the focus of recent literature has been on detection of mercury. Researchers have devised many novel methods to detect these at extremely low concentrations in environmental samples, down to the low µg/L range. However, this has not been tested using portable Raman spectrometers, which are usually less powerful and sensitive than benchtop counterparts. Some of the SERS systems that give remarkable detection limits (such as the silver NPs in $CoFe_2O_4$ shells modified with single-stranded DNA and single-walled carbon nanotubes on the NP surface) are very expensive and it is difficult to synthesise the materials in the large amounts needed for routine usage in the field. Such specific systems also have the drawback of having a low margin of error for synthesis, as slight errors in this complex model will significantly reduce reproducibility. Simpler SERS systems combining multiple techniques such as passive filtering, or adding an aggregation agent prior to measurements, may be more desirable in the future for fieldwork.

For pharmaceutical pollutants, specificity is key, as many pharmaceutical pollutants have similar chemical structures. This theoretically means they could be measured as a group but this would make it
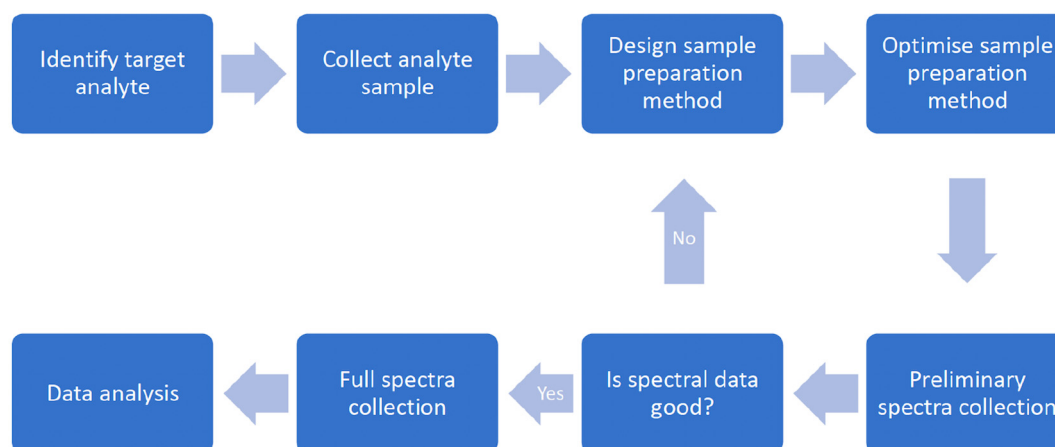
Fig. 2. Possible SERS workflow.

impossible to give data on individual compounds which is what is usually asked for by regulators. Pharmaceuticals may also mainly exist as their metabolites (e.g. a glucuronide form) in the environment, depending on the individual compound. This could again be dealt with by developing a robust spectral library for each compound and metabolite with detailed peak assignments. This would enable researchers to match peak profiles to sample spectra to determine whether it is the parent compound, or a metabolite.

Research has been performed to achieve detection at low concentrations using portable Raman spectrometers, but far fewer studies have been reported on using them in the field. As portable instruments have been demonstrated in the lab to have sufficient sensitivity, the next step is to carry out detection experiments in the field itself. SERS chips are a relatively inexpensive and convenient way to transport SERS systems into the field, and work well in combination with optical probes, which many portable Raman spectrometers have.

For EDCs, research using SERS is scarce, and mainly focused on clinical contexts. A natural evolution of this research area would be to focus on detection of such compounds in the environment but this has not happened to any great extent as yet. SERS has been proven to be as sensitive as conventional GC–MS, and much more efficient in terms of measurement time and sample pre-processing, but it is not yet as reproducible.

Perfluorinated compounds are an emerging pollutant of concern and the state of the literature is still developing. However, Raman spectroscopy and SERS are extremely appropriate for the detection of PFCs at low concentrations, due to PFCs having a unique chemical structure, mainly comprising of CF_2 and CF_3 moieties. This results in distinct Raman signatures, which theoretically should enable researchers to very easily discern whether an environmental sample is contaminated - if detection limits could be made adequate. Research to date has solely been using silver as the SERS metal substrate. Gold should be explored as a possible alternative, as it has SERS properties ideal for environmental sensing, such as higher inherent NP stability and synergy with excitation wavelengths that quench fluorescence. Another possibility is using silver NPs coated in an gold shell, forming bimetallic NPs, which have been applied successfully in experiments on other pollutant types.

For pesticides, a wider variety of types should be researched due to the favouring of different pesticides based on geographical region. SERS using portable Raman spectrometers is a natural fit for this application. Direct SERS experiments onto the unmodified environmental sample, such as tea leaves and fruit peel, have proven to be able to detect the presence of pesticides (Fang et al., 2015). Slightly more complicated sample processing such as extracting the pesticide compound (which would need to be done in the laboratory rather than the field) prior to SERS measurements yield a lower limit of detection. SERS is well on its way to becoming the standard in routine pesticide detection in the field.

TLC-SERS is an upcoming technique that is attractive for combining analyte separation with the sensing power of SERS; in this way TLC compensates for one of the weaknesses in SERS: the potential for non-target analytes to interfere in detection of a particular pollutant. Normally, analyte separation requires specific chemistry which cannot be feasibly applied outside of the lab or requires equipment that is not portable or is time-intensive, thus not suitable for field experiments. TLC-SERS as an analytical technique is well-suited for environmental detection projects. Although the limits of detection of recent works is not as competitive compared to the other environmental SERS publications in this review, TLC-SERS has the potential to be developed into a better sensing system with more time invested into its research. For example, the SERS NPs used in the papers cited are relatively simple; researchers could apply one of the many highly sensitive nanostructures for TLC-SERS that are currently reported in the literature, and could expect a similarly high degree of sensitivity.

6. Conclusions

Raman Spectroscopy boasts much higher efficiency than mass spectrometry in terms of sample pre-processing and measurement runtime. Measurements can be run in the field, an ability most mass spectrometry-based techniques lack. Crucially, when combined with Surfaced Enhancement techniques, Raman Spectroscopy can potentially match mass spectrometry in terms of sensitivity. The development of this latter point is however, quite variable at present and this is where the bulk of the current research is focused.

The groundwork has been done for developing SERS sensors to provide a sufficient Raman signal increase to detect a target analyte at environmentally relevant concentrations. However, this has mainly (but not exclusively) been tested in the lab using benchtop Raman spectrometers, perhaps with wireless capability for data processing. The next step is to adapt the method and SERS systems to be used in the field. Portable Raman spectroscopy and SERS haveing the potential to meet the demands set for performing real-time environmental water quality monitoring in the field, at concentrations low enough to detect pollutants at the concentrations that are thought to exist in the environment itself. Complex mixtures of compounds can potentially be dealt with via the development and use of spectral libraries of common pollutants While methodologies need to be optimised before the technique could become widespread there are an increasing number of studies that have used SERS to detect pollutants in the environment. The challenge for the future to develop and raise awareness of the potential benefits of SERS to environmental analyses.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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