# Extraction efficiency of four pesticides using the QuEChERS extraction method and analysis by HPLC/DAD

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# Populärvetenskaplig sammanfattning

Att pesticider används som ett skydd i jordbruket är ingen nyhet, och är en nödvändighet för att skydda odlingarna från diverse insekter, ogräs och mögel. Jord är en komplex matris, och leder till olika upptagningsförmågor av just dessa besprutningar. Ett löpande problem är avsaknaden av instrument där halter av pesticider kan mätas med hög noggrannhet, även vid låga koncentrationer vid analys. Metoder har tagits fram just för kunna göra dessa mätningar, där även mindre mängd lösningsmedel och billigare utrustning kan tillämpas. En sådan provberedningsmetod är QuEChERS - quick, easy, cheap, effective, rugged, and safe - och är högst populär just på grund av att lite lösningsmedel behövs, utrustningen är minimal och lättillgänglig, och kan göras relativt snabbt. I denna rapport har olika parametrar, mängd och typ av salt och sorbent, övervakats med QuEChERS-metoden med mål att se trender kring hur dessa parametrar påverkar extraktionseffektiviteten för fyra pesticider i jord. Dessa pesticider, imidacloprid, propiconazol, prallethrin och deltamethrin, kan särskiljas med hjälp av sitt log P värde, som är ett mått på en substans hydrofobicitet i dess oladdade form och anger jämviktskonstanten i en oktanol/vattenblandning. Med QuEChERS metoden, övervakades olika förhållanden mellan de två sorbenterna, opolär Nucleosil $C_{18}$ och polär $NH_2$, och saltet magnesiumsulfat med mål att kunna se trender kring vilket förhållande som ger bäst extraktionsutbyte med pesticiderna i fråga. Även observationer har gjorts kring hur en ökad sorbent- och saltmängd kan påverka extraktionseffektiviteten. Metoden går ut på att salta ut analyterna i provet som består av en blandning av vatten- och organisk lösning till organiska fasen, genom repulsion och en ökad hydrofobisk effekt. Efter övergången genomgår provet en upprening med sorbent för att säkerställa renlighet i provet för optimal analys, som utförs i HPLC-DAD.

Trender som kunde bemärkas var att $NH_2$ var den sorbent som utgav högst extraktionsutbyte för alla pesticider då den binder polära matrissubstanser som finns i jorden. Vid en ökad mängd av sorbenten $NH_2$ påvisades ett ökat utbyte för en av pesticiderna, deltamethrin. När $C_{18}$ användes som sorbent, kunde en minskning i extraktionseffektivitet för prallethrin, propiconazol och imidacloprid observeras, jämfört med $NH_2$. En extraktion med högre mängd salt visade högre utbyte för imidacloprid och deltamethrin, och en lägre visade högre för propiconazol. Prallethrin påvisade lika utbyten, oberoende av saltmängden. HPLC-DAD vid 235 nm var en lämplig analysmetod som gav hög selektivitet och detekterbarhet för var pesticid.

# Abstract

A cleanup step is essential from an analytical perspective, to improve the chance of quantification and to minimize interference. Pesticides in soil are a necessity is agriculture for survival of crops and protection from unwanted growth and pests. However, an ongoing problem is the lack of instruments where levels of pesticides can be measured with high accuracy, even at low concentrations during analysis. In this study, the extraction selectivity and efficiency of four different pesticides was observed with the quick, easy, cheap, effective, rugged and safe (QuEChERS) method coupled with high performance liquid chromatography-DAD. The sample consisted of four pesticides with different positive log P values in soil. The observed parameters for obtaining the highest extraction efficiency were amount and type of sorbent and salt. The two sorbents tested were the non polar Nucleosil $C_{18}$ and polar Nucleosil $NH_2$, with the aim to observe which of them gave a higher extraction efficiency. Magnesium sulphate is the salt that is used as a drying agent. A observation regarding the change in extraction efficiency with an increased sorbent and salt amount was also made. In terms of linearity and precision, the experiment was validated with a soil sample collected from LTH-parken in Lund. A matrix matched calibration curve were prepared for all analytes in question to estimate the recovery of pesticides after cleanup. From the method, it showed that $NH_2$ sorbent showed the highest extraction efficiency for all pesticides, because of its ability to adsorb the multitude of polar interference in the matrix. At an increased amount of the sorbent $NH_2$, an increased yield of one of the pesticides, deltamethrin, was detected. When $C_{18}$ was used as the sorbent, a decrease in the extraction efficiency of prallethrin, propiconazole and imidacloprid was detected compared to $NH_2$, due to a probable interaction between the analytes and the adsorbent. An extraction with 6 g $MgSO_4$ showed higher yields of imidacloprid and deltamethrin, and 4 g of $MgSO_4$ showed higher yields of propiconazole. Prallethrin showed equal yields, regardless of the amount of salt. HPLC-DAD at 235 nm was a suitable analyzing method that provided high selectivity and detectability for each pesticide.

# 1 Acknowledgement

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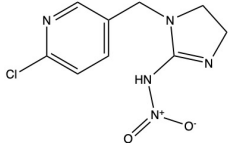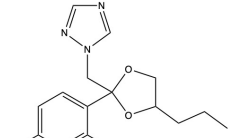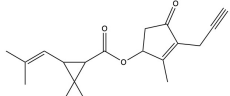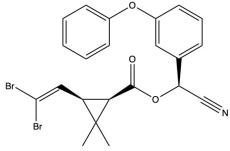
# Contents

# 2 Introduction

Pesticides are chemical substances used to kill pests, or in other cases rather control or repel them. Different types of pesticides include insecticides used to control a multiplicity of insects, herbicides for destroying weeds and unwanted growth, and fungicides to prevent mildew and mold growth (Nicolopoulou-Stamati, Maipas, Kotampasi, Stamatis, & Hens, 2016). They are widely used in agriculture and plantation sites and are a necessity for growth and survival of the crops. With the different interactions between analytes and soil and different interference, the residues from these pesticides are detected in divergent concentrations and are an adversity in an analytical perspective. Soil is a complex matrix to study. It contains so called soil organic matter, which consists of carbohydrates, free fatty acids, lignin and lipids to name a few components (Ahmed et al., 2015). A method where the pesticides can be accurately detected in soil is therefore vital to develop. One challenge has also been to find a relatively sustainable one where minimal amount of sorbent and cheaper equipment can be used. One method has been conducted in order to distinguish pesticides where these criteria are met, and it is the quick, easy, cheap, effective, rugged, and safe (QuEChERS) method.

Table 1: Overview of the pesticides used in this study
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| Pesticide name: | Class: | Type: | MW (Da) | Log P: | pKa | Structure: |
|---|---|---|---|---|---|---|
| Imidacloprid | Insecticide | Neonicotinoid | 256 | 1.2 | 11.12 | |
| Propiconazol | Fungicide | Triazole | 342 | 3.2 | 1.09 | |
| Prallethrin | Insecticide | Pyrethroid | 300 | 4.3 | 18 | |
| Deltamethrin | Insecticide | Pyrethroid | 505 | 6.2 | 10.65 | |

## 2.1 QuEChERS

QuEChERS is an acronym for quick, easy, cheap, effective, rugged, and safe and is a type of sample preparation method (Lehotay et al., 2007). It's a widely used preparation method used to perform pesticide analysis and is gravitated towards because of its low maintenance and low usage of solvents and sample. The method is also popular because of its ability of modification and optimization depending on the wanted results and the sample matrix one, and is noted to be a accurately method to use to analyze pesticide residues in food and agriculture samples (Anastassiades, Lehotay, Štajnbaher, & Schenck, 2003). It consists of two parts, a sample extraction step and a clean up step. According to the method, one should be able to analyze the finished sample from only the first step. However, the second sample clean up step is also performed as a precaution to obtain a cleaner sample. There are two versions of the QuEChERS method, the EN 15662 & Mini-Multiresidue and AOAC 2007.01., whereas the latter one is used in this study. The two versions essentially have the same course of action, however there are some differences. Both methods use magnesium sulphate, $MgSO_4$, as a dehydrating agent, but in the AOAC method, 6 g $MgSO_4$ is used and 1.5 g sodium acetate, NaOAc, is used as a buffering salt in the extraction step. However, in the EN method, 4 g $MgSO_4$ is used in conjunction with 1 g sodium chloride, 0.5 g NaCitrate dibasic sesquihydrate and 1 g NaCitrate tribasic dihydrate. Another difference is the amount of sorbent used in the extraction step, where 50 mg primary secondary amine, PSA, is used in AOAC and 25 mg PSA is used in the EN method (Musarurwa, Chimuka, Pakade, & Tavengwa, 2019). According to literature, the two methods works very similarly to each other (Lehotay et al., 2007), so the one with fewer components was chosen. The effect of NaOAc is not observed in this study, the amount of it added in the first step is in a 4:1 ratio. For 6 g $MgSO_4$, 1,5 g is added and for 4 g $MgSO_4$, 1 g NaOAc is added. The QuEChERS method does not cover the preparation of how to obtain a homogenized sample, they instead refer to other sources. The sample in question must therefore be previously homogenized to obtain a sample which represents the whole product, and improves the extraction efficiency of the desired analytes as it creates a bigger surface area. For a dry sample, like dried soil in this case, water should be added (*QuEChERS, About The Method*, n.d.). Without the water added to the sample, the interference would be present in the ACN-layer instead, which would make further cleanup difficult.

The partition of analytes from the high water content sample to the organic phase occurs through a simple salting out phenomenon. Essentially, when the salt concentration of an aqueous solution is increased, the solubility of non electrolyte substance in the solution will decrease. The dissolved anions in the solution will by a combination of electronic repulsion and an enhanced hydrophobic effect cause the salting out effect, and the hydrophobic compounds will therefore

have a greater distribution into the organic phase. The hydrophobic effect causes analytes to aggregate, and the bigger the analyte, the greater the aggregation will be since their interaction surface is bigger. Aromatic halogenated compounds will also contribute to higher hydrophobicity of the compound because of an interaction between the benzene's and the halogens electrons, creating a delocalised system (Hyde et al., 2017). The salting out phenomenon is visible after the centrifugation, as there will be four distinctive layers in the tube: 1. Organic phase, where the analytes have partitioned, 2. Solids from the sample, 3. Aqueous layer which contains for example polar interference from your sample. 4. Bottom layer contains undissolved buffer salts.

An adsorbent fills the role of cleaning a sample by adsorbing matrix co-extractives and unwanted particles onto it is surface, with the result of target analytes remaining in the solvent.(Tripathy et al., 2019). It is therefore important to observe the physical properties of the targeted analytes and pick an appropriate sorbent to increase extraction efficiency. Sorbents are efficient in a way that the do not leave any contaminant in forms of by-products. (Oshita & Jardim, 2014). In the official AOAC method, a 3:1 ratio between $MgSO_4$ and sorbent, primary secondary amine - PSA, is used in the cleanup step (Lehotay et al., 2007). The two observed sorbents in this study are the non polar Nucleosil $C_{18}$ and polar Nucleosil $NH_2$. Nucleosil $NH_2$ is a weak anion exchange sorbent which causes it to remove interference that can form hydrogen bonds, such as sugars, organic acids and fatty acids. Nucleosil $C_{18}$ is a non polar sorbent that will adsorb non polar interference. CCB, Graphitized carbon black, is also a commonly used sorbent for the method and is gravitated towards when the sample contains pigments and sterols, but will not be used in this study. (Wilkowska & Biziuk, 2011),(McDonald, Bouvier, & Division, 1995).

The buffer salts control pH, buffering helping to stabilize pH sensitive analytes. Magnesium sulfate ($MgSO_4$) is a dehydrating agent added to absorb water in both the extraction and cleanup steps. In the extraction step, it also increases the ionic strength of the aqueous mixture and induces phase separation for acetonitrile and water and for the analytes to partition to the organic phase. (Wilkowska & Biziuk, 2011).

## 2.2 High performance liquid chromatography.

Using a $C_{18}$ column for a reversed phase chromatography offers a hydrophobic interaction between analytes and column. The pesticides used in this study differentiate in log P value, a parameter that indicates the degree of a compound's hydrophobicity. This value is the equilibrium constant of a compound in its un-ionized form after it is placed in a mixture of water and n-octanol. A positive log P value indicates that the compound is more soluble in n-octanol and thus has more hydrophobic nature. A $C_{18}$ column will be used for a reversed phase chromatography since it offers a hydrophobic interaction between the analytes with positive log P values analytes and column. Therefore, the analytes will elute in the order of their log P value (Amézqueta, Subirats, Fuguet,

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Rosés, & Ràfols, 2020). Acetonitrile is an aprotic polar solvent, it lacks an acidic proton. It's also easily separated from water, and miscible in water. For this study, acetonitrile was chosen over methanol, another popular solvent, since acetonitrile in water has a higher elution strength compared to methanol in water. Since the log P values of the compounds increase, the solvent needs to be strong enough to be able to elute the analytes.

## 2.3  The parameters in this study

The power of the sample preparation method QuEChERS lies in it is ability to shape the method according to the chemical properties of the analytes. Depending on what factors that are observed, the method can be configured to meet the needed criteria. But, with a versatile method like QuEChERS, some hindrance is bound to appear. One apparent problem is how the majority of the literature does experiment on a big set of pesticides. This can become difficult for someone who might be looking for the result of QuEChERS for a group of analytes with specific properties. In this study, the effect on extractability of four substances with different log P and pKa properties (Table 1) in soil will be monitored in consideration to the amount of salt and sorbent. The effect of an increase in sorbent and salt amount on extraction will also be monitored. The two adsorbents will be compared to draw a conclusion as to which of them will result in a higher yield , and how an increased amount will affect the recovery. The two different adsorbents are non-polar Nucleosil $C_{18}$ and polar Nucleosil $NH_2$. The effects of the two sorbents are observed separately. The sample preparation method will be tested by running the cleaned up samples in HPLC-DAD.

# 3 Material and method

## 3.1 Chemicals and reagents

The pesticides used in this study - Prallethrin (PRA), Propiconazol (PRO), imidacloprid (IMI) and Deltamethrin (DEL) were purchased from Sigma-Aldrich (St. Louis, MO, USA). Three sorbent amount (10 mg, 25 mg, 50 mg) are tested, and two salt amounts are tested, 4 g and 6 g $MgSO_4$.

HPLC grade acetonitrile (ACN) was purchased from VWR (Radnor, PA, USA) and MILLIQ water was produced in the laboratory using a Gradient A10 Milli-Q System (Millipore, Bedfore, MA, USA). Formic acid was purchased from Sigma-Aldrich.

## 3.2 Preparation of pesticide stock solutions and calibration standards

The pesticide standard were prepared at 1000 mg/L. All were dissolved in isopropanole except for propiconazole which was dissolved in ethanol. The solutions were kept in -20°C . Calibration standards were prepared in a range of six concentrations: 10, 15, 20, 25, 30, 35 mg/L in a 1:1 ACN/Milli Q water solution.

## 3.3 Preparation of soil sample

An amount of 1 kg soil from LTH-parken in Lund was collected from a depth of 10-20 cm. Big pieces of bark and insects were removed and the soil was dried in a 50°C oven for approximately 1 h, homogenized and sieved (2 mm mesh) and stored in an air tight jar before use.

## 3.4 Sample preparation method (QuEChERS)

In the extraction part of the method, 3 g of soil and 12 ml $H_2O$ are added to a 50 ml centrifuge tube and to it, 15 ml of acetonitrile acidified with 1% acetic acid is added and the sample is spiked with 500 µL of each pesticide at 1000 mg/L and blended to create a homogeneous sample with pH 4.5. To it, 6 g $MgSO_4$ and 1.5 g NaOAc are added to the mixture and mixed vigorously immediately for 1 minute. The tube is centrifuged at 5000 rpm for 5 minutes. The supernatant is collected for further clean up.

After the sample extraction step, 2 mL of the supernatant, upper layer organic phase, is transferred to a 25 ml centrifuge tube. To it, 150 mg $MgSO_4$ and 50 mg Nucleosil $NH_2$ is added. The tube is vortexed for 1 minute and centrifuged at 5000 rpm for 5 minutes. The supernatant is then collected, and analyzed in HPLC-DAD.

## 3.5 Instrumental analysis using High performance liquid chromatography - diode-array detector

The HPLC-DAD analysis of the samples were performed on an Agilent 1100 LC system (Agilent Technologies, Santa Clara, CA, USA) consisting of a G1311A QuatPump, G1329A ALS, G1379A Degasser, G1316A column oven). The mobile phase consisted of Milli-Q water in 0.1% formic acid (A) and acetonitrile (ACN) in 0.1% in formic acid (B) (Acosta-Dacal, Rial-Berriel, Díaz-Díaz, Bernal-Suárez, & Luzardo, 2021).

The gradient, starting at 20% B was increased to 100% in 10 minutes, kept there for 6 minutes and returned to the initial conditions in 1 minute with a postrun time of 1 minute, resulting in a total run time of 18 minutes. The wavelength chosen for the analysis was 235 nm. The column temperate was set to 55°C, injecton volume was 15 µL and the flow rate was set to 1 ml/min. The auto sampler system in the HPLC was used to inject samples and a needle wash in ACN was performed before each injection.

The column used was a Kromasil 100-5-$C_{18}$ with dimensions 4.6 x 150 mm, with particle size of 5 µm and pore size 100 Å.

# 4 Results and discussion

The QuEChERS method was successfully performed on four pesticides with different log P values, as an attempt to find a pattern between salt and sorbent content and extraction efficiency.
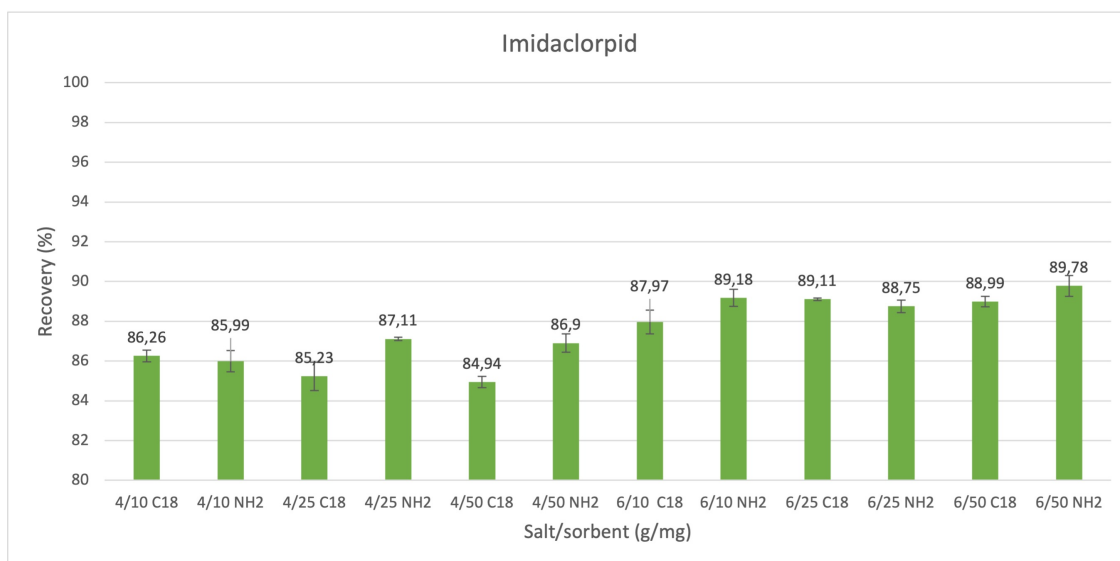
## 4.1 QuEChERS

### 4.1.1 Imidacloprid



Figure 1: Recovery of imidacloprid extracted from spiked soil at varying amounts of salt ($MgSO_4$) and sorbents ($C_{18}$ and $NH_2$), error bars represent standard deviations for 3 replicates.

Looking at the first eluted pesticide, the basic compound imidacloprid has a pKa value of 11,2. For the given extraction conditions of this method at pH 4,5, the compound will be in it is protonated form with a positive charge. It also has the lowest log P value out of the four compounds with a value of 1.2, and is therefore expected to elute first as it is the least hydrophobic and will have the shortest retention time. Since the compound has a positively charged nitrogen, the likelihood of it partitioning into the organic phase during the extraction step is lower. Thus, resulting in the concentration being lower than if it was uncharged. The observed recovery values are relatively close to each other with a small STD. When comparing the two different salt amounts, there is an overall trend of higher yield with 6 g compared to 4 g. Looking at salt amount, the biggest observed yield difference for $C_{18}$ was 50 mg of the sorbent, where 6 g salt had a 4 % higher recovery than 4 g. When looking at $NH_2$, 10 mg gave the biggest difference in yield, 3%. There was no clear pattern as to which sorbents gave a higher yield, as no sorbent had a higher recovery than the other. There is no clear pattern between increasing sorbent amount and increasing yield. When looking at $C_{18}$

and 4 g salt, there is actually a decrease of 0.5-1 % as the sorbent amount increases. A trend could be observed that with an increased salt amount, the recovery of imidacloprid increased as well. This could be due to a higher electronic repulsion and higher hydrophobic effect during the partitioning, leading to an elevated probability of partitioning.
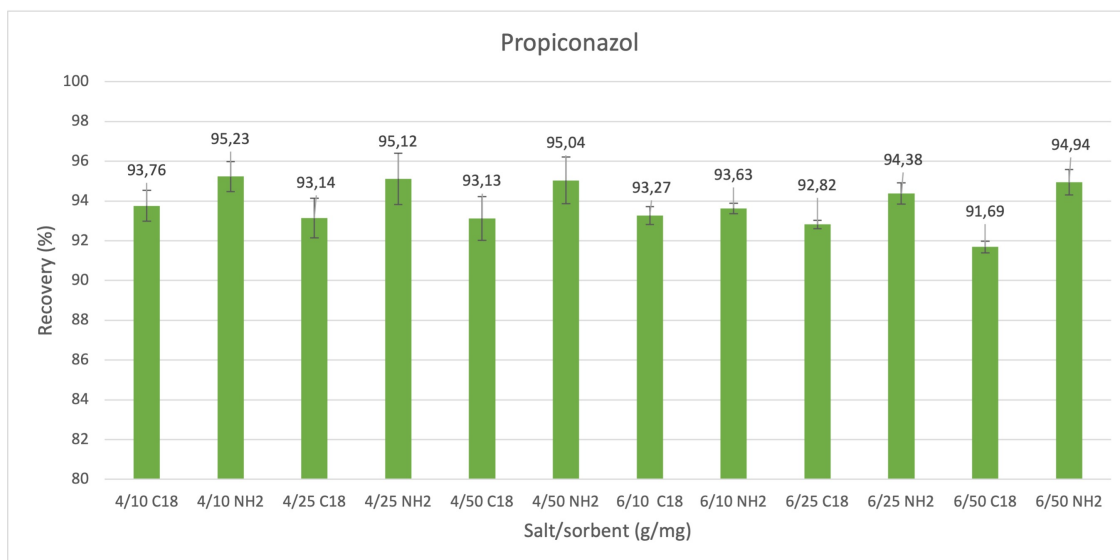
### 4.1.2 Propiconazol



Figure 2: Recovery of propiconazol extracted from spiked soil at varying amounts of salt ($MgSO_4$) and sorbents ($C_{18}$ and $NH_2$), error bars represent standard deviations for 3 replicates.

Propiconazol, with a log P of 3.2, has a lower pKa than Imidacloprid, of 1.09. Since the pH of the sample is 4.5, it means that the compound will be in an uncharged form. This compound has two chlorine molecules substituted on it is benzene ring. The effect of this is a delocalised system of electrons which makes this compound very insoluble in water. Looking at the results for Propiconazol, it is the compound with the highest yields overall, with the lowest value being 91,7% (6/50 $C_{18}$). The recovery of the compound is higher for all the compositions with $NH_2$ as sorbent, with a range of 1-3 % higher compared to $C_{18}$. For 4 g salt, neither of the sorbents give a higher recovery when the sorbent amount is increased. However, for 6 g salt, there is a slight higher recovery for $NH_2$ with increased sorbent amount, with an increase of 0.5% per amount. The opposite goes for $C_{18}$, where the recovery decreased with 1% when the sorbent amount increased. The relatively high log P value and the halogenated benzene ring gives ground for the very high recovery of propiconazole.
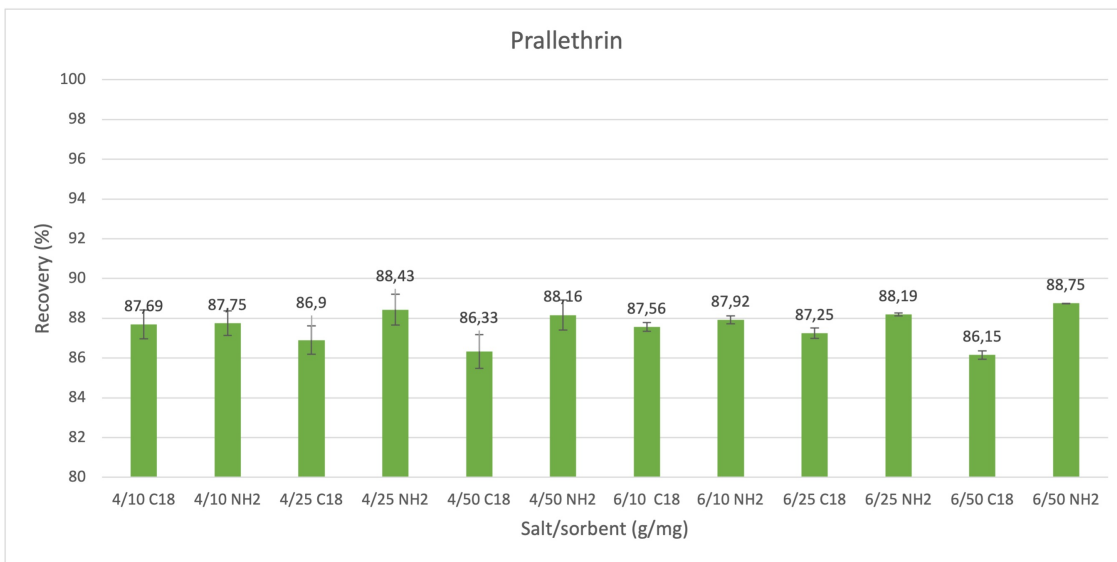
### 4.1.3 Prallethrin



Figure 3: Recovery of prallethrin extracted from spiked soil at varying amounts of salt ($MgSO_4$) and sorbents ($C_{18}$ and $NH_2$), error bars represent standard deviations for 3 replicates.

Prallethrin, with a pKa value of 4.3 and log P of 18, will be present in a uncharged form. Because of this, this compound will have a high likeliness of partitioning to the acetonitrile phase. Furthermore, the lower log P value is another indicator to this. When looking at the recovery of prallethrin, it is partially consistent with the theory. The recovery of the compound are in a range between 86-88 %, around the same range as imidacloprid, even if the compound is uncharged and with higher molecular weight and a higher log P value than imidacloprid. The recovery of the compounds is, like propiconazole, higher for all the compositions with $NH_2$ as sorbent, with a range of 0.5-2 % higher compared to $C_{18}$. Looking at sorbent amounts, for 4 g, an increase in $C_{18}$, a trend of decrease in the yield, with about 0.7% as the amount increased was observed, indicating that the analyte might be adsorbed to $C_{18}$. There is no real pattern for $NH_2$ for this salt amount, as it decreases first and then increases. For 6 g salt, the pattern for the two sorbents are similar to as 4 g salt. The recovery means for the two salt amount differ by 0.1%, indicating that it might not have a big effect on the extraction efficiency which amount is used.
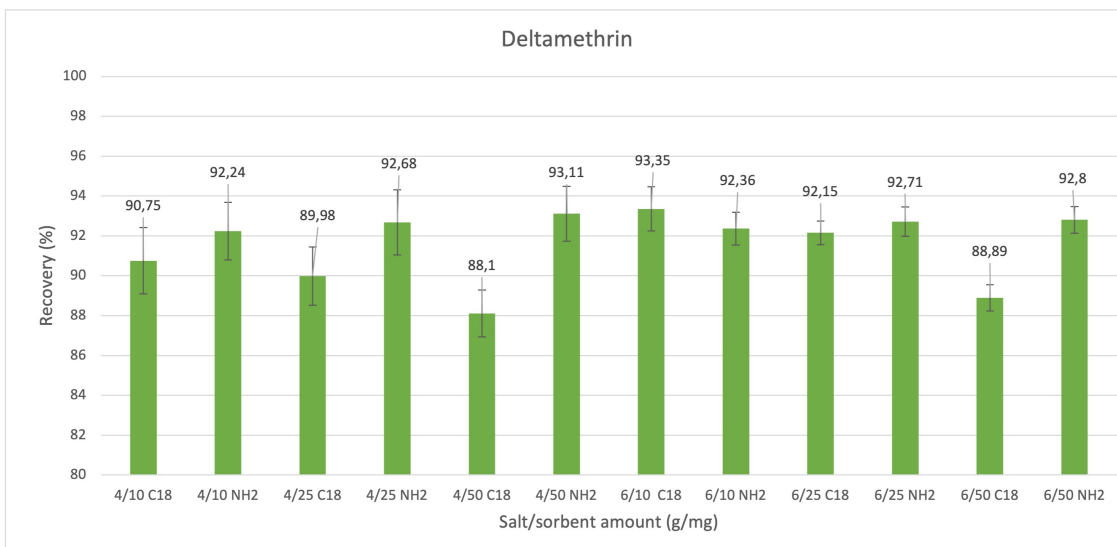
### 4.1.4 Deltamethrin



Figure 4: Recovery of deltamethrin extracted from spiked soil at varying amounts of salt ($MgSO_4$) and sorbents ($C_{18}$ and $NH_2$), error bars represent standard deviations for 3 replicates.

Deltamethrin is the compound with the highest log P value and highest molecular weight. It also has a pKa value of 10.65, leading to it being protonated and therefore positively charged under the circumstances of the elution. It has the highest molecular mass and is the compound with highest log P value, which gives it good conditions for high recovery. The recovery is relatively consistent with the theory, with a recovery range was between 88-93%. It is noted to be an overall higher when $NH_2$ sorbent is used, where it has 3-5 % higher recovery than $C_{18}$ except for when 6/50 mg $C_{18}$ sorbent was used, there $C_{18}$ had 1 % higher recovery than $NH_2$. The recovery is slightly higher with 6 g salt than 4 g salt. Deltamethrin's observed yields are higher, in comparison to prallethrin, two compounds with similar structures. Since deltamethrin has a greater molecular weight than prallethrin, the tendency of it aggregating is greater as well, leading to a higher probability of it partitioning to the organic phase than prallethrin, which agrees with the result. $NH_2$ is the more appropriate sorbent to use with this compound. Since deltamethrin has a charge, this could mean that the recovery is not as high as it could've been with a neutral charge to it. The same trend that could be observed with imidacloprid could be dome with deltamethrin, that with an increased salt amount, the recovery increased as well, due to a higher electronic repulsion and higher hydrophobic effect.
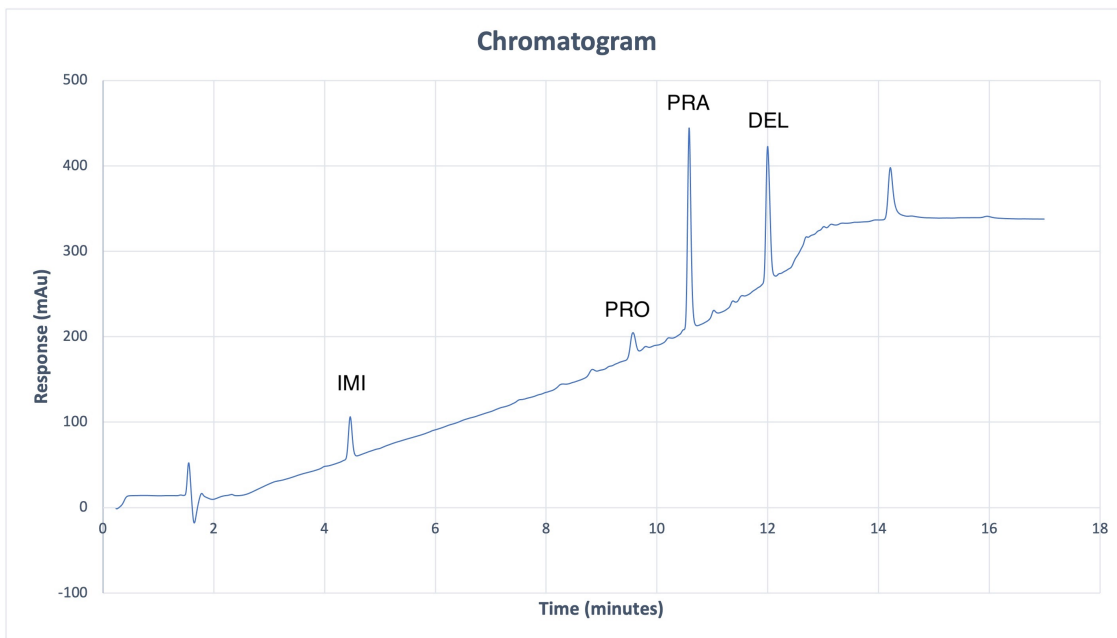
## 4.2 HPLC



Figure 5: Chromatogram of the pesticides at 35 µg/ml. The retention times of the pesticides are 4.47, 9.57, 10.58 and 11.98 min, respectively. (n=3)

All the pesticides used in this experiment have a positive log P value, indicating being more soluble in organic solvent rather than an aqueous one. The compounds are expected to elute in the order of their log P values, with the least hydrophobic eluting first, which can be seen in Figure 5. Since the log P increased for the pesticides, it was important that the mobile phase composition was more on the hydrophilic side to retain the analytes.

Peak splitting was an issue for IMI when calibration standard were prepared in a solution of 100% ACN. This problem was fixed by preparing it in a 50/50 ACN/H–2O and decreasing the injection volume from 20 µL to 15 µL.

# 5  Conclusions

The QuEChERS method is an exceptional method to use for a high recovery for a multitude of pesticides, regardless of properties and sample matrix. It was performed on four pesticides with different log P and pKa values with the aim to observe the extraction efficiency when amounts of salt and sorbents and altered. The analysis was done in HPLC-DAD for an overall high recovery of all four pesticides. No conclusions about significant differences in extraction yield could be drawn due to limited statistical data. The highest recovery was observed at 6 g MgSO$_4$ + 50 mg Kromasil NH$_2$ for all pesticides. For NH$_2$, if the salt amount is decreased to 4g, the recovery of imidaclorpid decreases with 2-3 % for all three sorbent amounts, while the other pesticides recovery remains the same. An increase in NH$_2$ sorbent did not result in an increased extraction efficiency, regardless of salt amount. For $C_{18}$, 6 g MgSO$_4$, showed higher recovery than 4 g, expect for propiconazol. An increase in the $C_{18}$ sorbent amount also resulted in a decrease in recovery for all pesticides, due to a probable adsorption of the analytes. Imidacloprid and prallethrin has close observed recoveries, while prallethrin is a neutral compound with three times higher log P value than the charged imidacloprid. The delocalised system of electron in imidacloprid and propiconazol could therefore have a big impact on the hydrophobicity of it, and enhance the probability of it partitioning during the extraction. Regarding $C_{18}$ as a sorbent, it, in conjunction with 6 g MgSO$_4$, showed higher recovery than with 4 g salt. The trend were the imidacloprid recovery decresed with a decrease in MgSO$_4$ corresponds with $C_{18}$ also, with 2-3 %. An observation is that the yields of the two compounds that were charged, imidacloprid and deltamethrin, could be due to a lower tendency of partitioning to the organic phase. The observed recoveries of the two charged compounds, imidacloprid and deltamethrin, is higher with an increased salt content, due to a more favorable partition when the electronic repulsion is increased. Considering charged analytes of similar mass, a higher log P value has a higher distribution into the organic phase. This could be seen with prallethrin and propiconazol, with NH$_2$ as a sorbent, where prallethrin had a tendency of a higher recovery. With $C_{18}$, the opposite was noticed, propiconazol had a higher recovery. Another factor that should be taken into consideration is the solvent. Acetonitrile is a polar solvent that is more effective on analytes with lower log P values. With neutral compounds that have higher log P values, a non polar solvent is more suitable. This observation could play a roll in the recovery of the neutral compounds of higher log P, since the prerequisites are not optimal for the highest possible recovery.

# 6   Future aspects

In this experiment, the sorbents were tested separately, but there is a possibility that a combination of sorbents perform even more efficiently, to gain the most of the sorbents unique abilities. Another way to perfect this method is to see it form a sustainability point of view. The amounts used in this method are small, but could always be improved. If the method could be scaled down but still contain it is high extraction efficiency, it would mean less wastage and less impact on the environment. This aspect would also benefit the economical point of view, as lower usage of sources means lower costs.

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