



# Additives Depletion by Water Contamination and Its Influences on Engine Oil Performance

A. Al Sheikh Omar<sup>1</sup> · F. Motamen Salehi<sup>1</sup> · U. Farooq<sup>2</sup> · A. Morina<sup>1</sup>

Received: 9 February 2024 / Accepted: 27 May 2024  
© Crown 2024

## Abstract

Water enters engine oil in different ways and moves in the lubrication system causing an increase in wear, oil degradation and additives depletion. It has been proposed that water in the lubricants can transfer from dissolved to free phase leading to additives depletion in the oil. Different additives in the lubricants can easily latch to water molecules forming reverse micelles. The separation of reverse micelles from the oil causes additives depletion. This experimental and analytical study aims to investigate how the separation of free water above the saturation level can diminish the efficiency of additives in engine oils. The effect of varied levels of water on oil performance and its additives was investigated in this study. A new saturation method was used to determine the water saturation level in engine oil at different temperatures. The results reveal a decrease in additive concentration with increased separation of free water from the oil. Free water separation from engine oil is expected to reclaim the tribological performance, however, the results demonstrate that tribological performance after the separation of free water from the oil has been affected. The study showed not only does the removal of free water diminish the efficiency of additives due to additives depletion ( $\approx 10$  wt%), but also the remaining dissolved water which is  $\approx 2600$  ppm can also affect wear and tribofilm chemistry. The results prove that two main mechanisms influence oil performance expressed as additives depletion by free water and remaining dissolved water.

**Keywords** Water saturation · Dissolved water · Wear · Additives depletion

## 1 Introduction

Water is one of the most destructive contaminants in engine oil after soot [1–3]. Water in engine oil causes a host of problems such as accelerating metal surface fatigue, increasing wear, producing corrosion, reducing film thickness, and inducing oil oxidation and additives depletion [2–6]. Water enters the engine oil in different ways and moves in the lubrication system in several physical and chemical states [7]. The most common sources of water in engine oil are moisture absorption from the air, water as by-products during the combustion and neutralization processes, leakage from heat exchangers, moisture condensation due to changes in atmosphere temperature, and free water entry during the

oil changes [7]. Water in lubricants is found in three different phases. Dissolved water when the water level in the oil is under saturation level. The molecules of dissolved water disperse in the engine oil in very small invisible sizes. When the amount of water exceeds the saturation level or the level that water can be dissolved, the oil loses its ability to dissolve more water resulting in an emulsified phase. As water content increases in the oil, the extra-water over the emulsified water level in the oil separates, forming free water. Emulsified and free water are widely recognised as particularly detrimental phases, significantly impacting lubrication systems and contributing to subsequent failures [8].

Different types of lubricants can manage different levels of dissolved water depending on the physical and chemical properties of the oil and its additives [4]. Dispersant/detergent additives disperse water molecules in the oil and prevent the formation of free water droplets. These additives influence the character of mineral oil to hold the water at different phases in terms of solubility and emulsion [9]. Dissolved water in oils could also be influenced by factors such as relative humidity, pressure, additives, and temperature [7,

✉ A. Al Sheikh Omar  
menaals@leeds.ac.uk

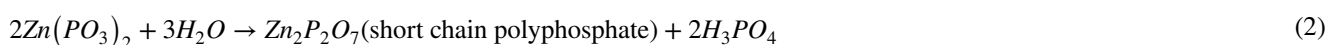
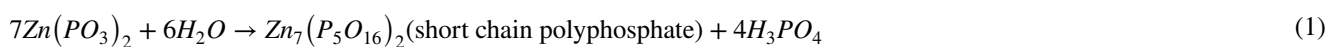
<sup>1</sup> School of Mechanical Engineering, Institute of Functional Surfaces, University of Leeds, Leeds, UK

<sup>2</sup> Racor Filter Division Europe, Parker Hannifin Manufacturing Ltd, Dewsbury, UK

9, 10]. According to Henry's law, the relationship between water content in oil and the amount of water in the air is linearly proportional [11]. Henry illustrates the varied levels of dissolved water in oils that contain different additives [10]. It is commonly agreed that water concentration in automotive oils does not have to exceed 0.2 wt%. The water concentration in the drain oil was found to be typically below 1 wt% and variations are widely seen in several studies [6, 11].

The hydrolysis effect on lubricants has been considered the main factor contributing to engine oil's chemical breakdown in the presence of water [2]. The physical and chemical stability of engine oil is threatened by even a small amount of suspended water. Water can hydrolyse, transform, and wash additives out of the lubricant [2]. It is known that water has a density higher than the engine oil. Excessive water beyond the saturation level will result in separation, potentially causing the removal of additives from the oil due to the presence of free water [12]. Dispersants and detergents in oils are used as the first barrier to protect the oil from water contamination. Water, as a polar molecule, is similar to oil additives that have polar heads. The heads of polar additives latch onto water molecules and surround them, forming reverse micelles. The non-polar tails of additives allow the additives to dissolve easily into the oil. When the water content in the oil increases, more reverse micelles are generated until they reach a level where the water amount overwhelms these additives and free water will separate [9]. Considering this, it could be assumed that extracting water molecules through filtration or separation, particularly as free water encapsulated by detergent, dispersant, or other additives, can inadvertently lead to the removal of these additives from the oil, however, this is not yet demonstrated experimentally.

Dissolved water in the oils diminishes the additives' performance and promotes corrosion. Water destroys the Zinc dithiophosphate (ZDDP) additive, which is referred to as antioxidant and antiwear additive, when it reacts with water at a temperature of 60 °C and above, resulting in increased wear [13, 14]. Rounds [14] suggested that ZDDP decomposition occurred not only by thermal decomposition but also due to the hydrolysis process. Fuller et al. [15] showed that long-chain phosphates, which result from the decomposing of adsorbed ZDDP on rubbing surfaces, hydrolyse these long chains in the presence of water, causing the formation of short-chain polyphosphates and phosphoric acid as described in Eqs. (1) and (2) [16–18].



Water influences the interfacial chemistry of ZDDP tribofilm formation, ZDDP adsorption and tribofilm adhesion to metal surfaces resulting in increased wear [19]. The formation of tribofilm can be influenced by the high polarity of water molecules. Water molecules attach to the metal surfaces and prevent additives from forming tribofilm [20]. The PAO lubricant containing 1 wt% ZDDP was investigated in the existence of 1 wt% water. The results demonstrated an increase in wear [20]. Parsaeian et al. [21] studied the effect of humidity conditions on wear depth with different relative humidity levels. The results revealed an increase in wear depth with a higher level of humidity. Parsaeian et al. [22] also investigated different levels of water 0.5, 1.5 and 3 wt% in the oil. The results reported an increase in wear depth and a decrease in tribofilm thickness with higher water concentration. Cen et al. [23] reported that adding water or adsorbing more water from humid air increases wear. The results agreed with the theory of the hydrolysis effect of ZDDP tribofilm that water can decay the stability of tribofilm by reducing tribofilm adhesion on metal surfaces [24]. Dorgham et al. [25] demonstrated that water in the oil causes a delay in the formation of tribofilm ending in the formation of short-chain phosphates.

The water is rigorously mixed into the engine oil and the lubrication fluid is pumped through the engine will have different water phases. While free water separation occurs when it surpasses the saturation level, it remains uncertain whether the oil can perform similarly to fresh oil after the separation of free water or not. This is due to additional factors, such as additives depletion caused by water or the presence of remaining dissolved water, which can also impact the functionality of the oil. The intent of this study is to understand how separating free water and remaining dissolved water affects the tribofilm chemical composition and tribological performance of engine oil.

## 2 Materials and Methods

A fully formulated oil (FFO) with a viscosity grade of 15–40 W was used to investigate water depletion in engine oil in this paper. The physical and chemical properties of this oil are presented in Table 1. The inductively coupled plasma (ICP-AES) technique was used to measure the additive elemental concentration in the oil samples at Oil Check Laboratory Services Ltd, UK according to ASTM D5185 standard [26]. Some primary elements (Table 1) such as zinc (Zn), phosphorus (P) and sulphur

**Table 1** Physical and chemical properties of fresh engine oil

Details	Parameters
Density at 15 °C (g/ml)	0.874
Kinematic viscosity at 40 °C (mm <sup>2</sup> /s)	113
Kinematic viscosity at 100 °C (mm <sup>2</sup> /s)	15
Flashpoint (°C)	215
Total base number (mgKoH/g)	10
Zn concentration (ppm)	1306
P concentration (ppm)	1158
S concentration (ppm)	6366
Ca concentration (ppm)	1332
Mg concentration (ppm)	941

(S) originate from the antiwear compound (ZDDP). However, S and P elements could also come from dispersant/detergent compounds such as sulfonates and phosphonates [27]. Calcium (Ca) and magnesium (Mg) come from detergents, for example, calcium sulfonates and magnesium sulfonates, respectively [28, 29]. Other additive elements were detected at low levels (< 30 ppm) in the oil, for instance, molybdenum (Mo), silicon (Si) and sodium (Na). Distilled water was used in saturation tests and tribological experiments. Coulometric Karl Fisher (KF) Titrator (Mettler Toledo Ltd, USA) was used to measure the water content in the engine oil samples according to ASTM D6304 standard [30]. Fourier-Transform Infrared Spectroscopy (FTIR) manufactured by PerkinElmer was conducted to monitor the formation of any degradation by-products of tested oil samples [31]. KF and transmission FTIR measurements were repeated three times and the average of the results was calculated. To study the additives depletion in the oil, the water was removed from

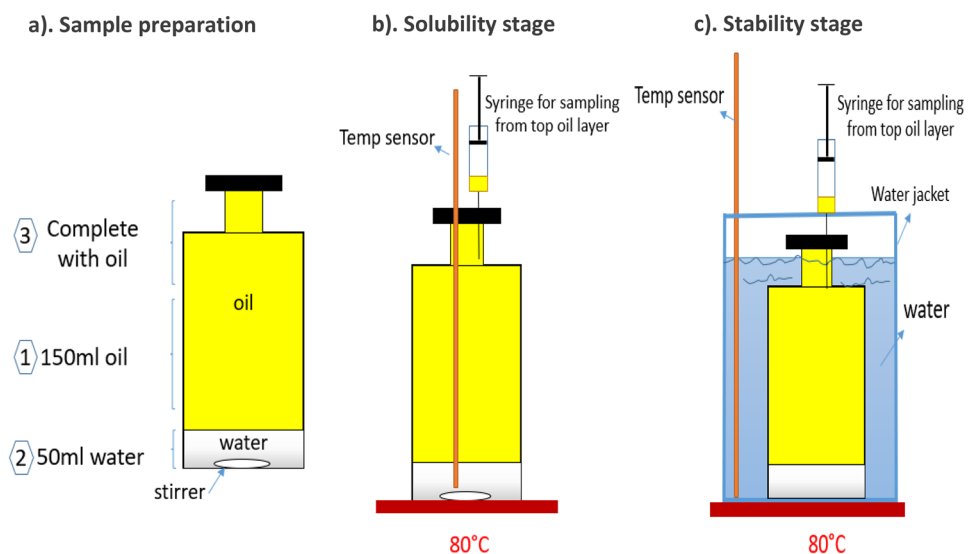
oils by centrifugation at a speed of 12,000 rpm and a temperature of 25 °C for 1 h.

## 2.1 Water Saturation Method

There is currently no standardised method for determining the water saturation level in engine oil. In this study, the preparation of the saturation test was devised based on the SAE J1488 standard [32]. While the SAE J1488 standard is conventionally applied to assess water saturation levels in fuel, adjustments were made to experiment periods for its application to engine oil. The saturation experiment is divided into three main stages as reported in Fig. 1. The effect of different factors on the water saturation test is discussed in this study. These factors include the effect of the stirring process and time on the water saturation test in the engine oil. The saturation experiment stages are described in detail as follows:

**(a) Sample preparation:** This stage is based on the SAE J1488 standard [32]. A glass bottle with a capacity of 250 ml was used in the saturation experiment. The bottle was washed before the test with distilled water and dried thoroughly. The 150 ml of the oil was placed into the dried bottle, and a small magnetic stirrer was inserted into the oil. A syringe fitted with a long needle was used to gently inject 50 ml of distilled water underneath the oil after removing the air bubbles from the syringe. Finally, the glass bottle was filled with engine oil, which will guarantee no water in the top oil layer was contaminated during test preparation. The bottle was fully sealed during the test. There were two open holes on the top, the first open hole was used for the temperature sensor surrounded by the rubber. The second hole was closed with a rubber cap and is used for sampling as described in Fig. 1a.

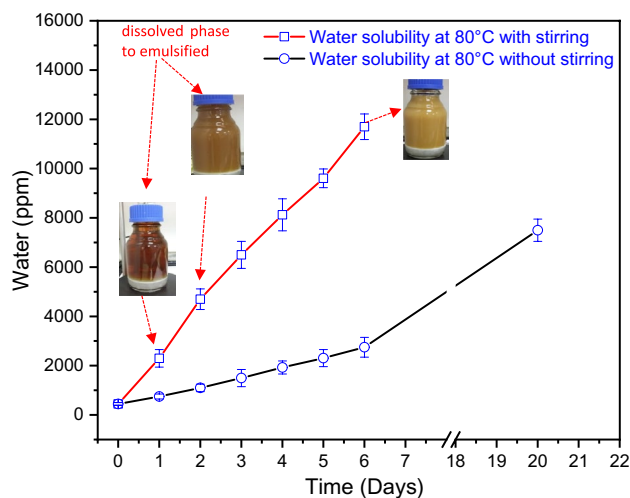
**Fig. 1** Schematic images of water saturation method in the oil. **a** sample preparation to create two separated layers of water and oil, **b** water solubility stage at 80 °C applied with stirring of 100 rpm, **c** stability stage was designed to stabilise the water in oil and separate any extra-water which cannot dissolve in oil at a fixed temperature (no stirring was used in this stage)



**(b) Water solubility:** This stage is designed to discover water solubility in the oil over time. Two water solubility tests were run under different conditions, in the first test, the temperature was fixed at 80 °C over time without stirring. The second test used both the temperature at 80 °C and magnetic stirring of 100 rpm as shown in Fig. 1b. The lowest stirring speed of 100 rpm was applied to avoid agitation of the oil–water interface and the vortex as a result of stirring. The results, as reported in Fig. 2, show the increase in the level of water in engine oil progressively over time under both conditions. The results show that the stirring accelerates the solubility of water in oil. For the water solubility test with stirring, as reported in Fig. 3, the oil appearance indicates that water in the oil becomes emulsified after 48 h and reaches the milky state after 72 h. The water solubility test for the oil without stirring takes a longer time to reach the milky state, as shown in Fig. 2. The water solubility stage proves that water does not stabilise at saturation level even without stirring. Therefore, an additional action is required to find the stable stage where the oil can hold

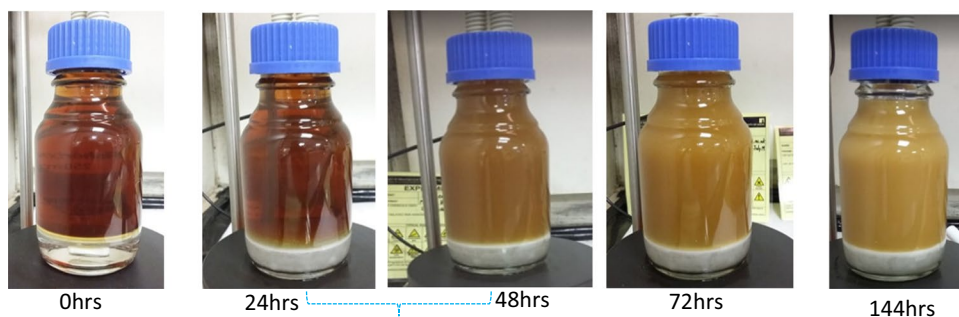
only the dissolved water. The next stage will determine the saturation points at a fixed temperature.

**(c) Water stability stage (saturation level):** The oil appearance, as shown in Fig. 3, confirmed that water in oil before 48 h transferred from dissolved state to emulsified state (cloudy). After reaching the emulsified state (48 h), the oil bottle was settled in the water bath at a fixed temperature. In this stage, the bottle was placed in a water bath at 80 °C without stirring to guarantee homogenous heating surrounding the test bottle as explained in Fig. 1c. The water in oil during this stage was measured over time until it reached the stable content of water in oil (Fig. 4), which is called the saturation point. After calculating the water saturation test at 80 °C, the water bath temperature was set at 60 °C to determine the saturation level at 60 °C. The same process is repeated with a fixed temperature of the water bath at 40 and 20 °C, and the water level was monitored over time until it reached a stable level (Table 2). To calculate the water saturation level at each temperature, the mean values (the

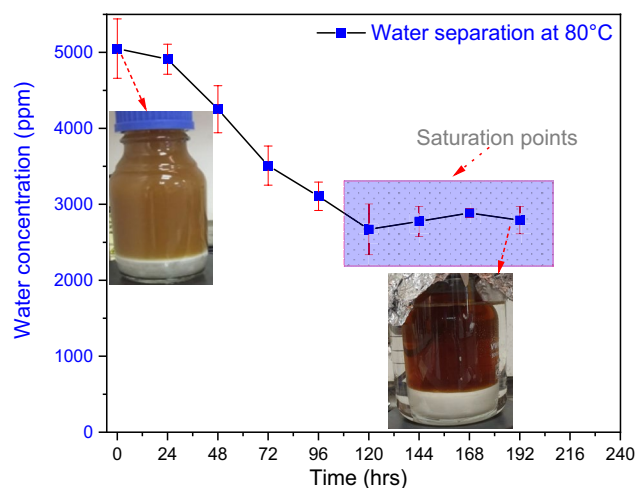


**Fig. 2** Water solubility in oil at 80 °C with stirring and without stirring

**Fig. 3** Oil appearance develops from dissolved water (transparent), as shown in 0 h and after 24 h, to an emulsified state (cloudy) after 48 h and reached the milky state of oil after 72 h



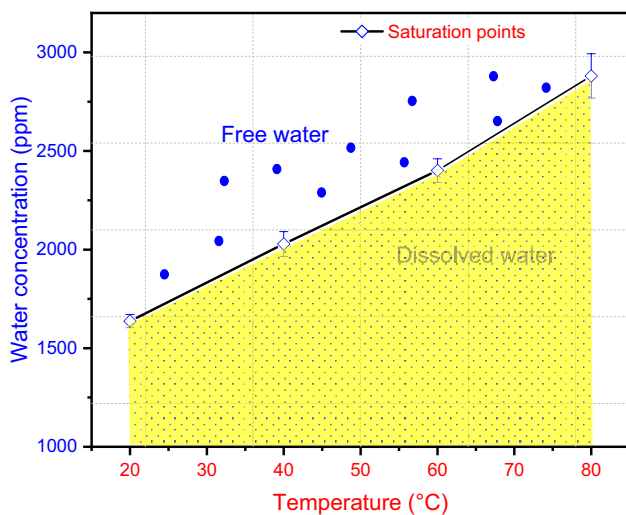
Transition from dissolved state to emulsified state occurs at < 48 hrs



**Fig. 4** Water stability test after the test reached the emulsified state moved to bath-temperated water to obtain the saturation points at 80 °C

**Table 2** Water readings (ppm) at the fixed temperature at the stability test over time, ± standard deviation was calculated from the mean

Time (hrs)	Fixed test temperature		
	60 °C	40 °C	20 °C
0	2881 ± 88	2400 ± 212	2077 ± 146
24	2284 ± 316	2021 ± 160	1734 ± 130
48	2509 ± 253	2045 ± 78	1626 ± 66
72	2527 ± 218	1968 ± 4	1624 ± 76
96	2447 ± 153	2030 ± 113	1654 ± 146
120	2400 ± 212	2077 ± 146	1647 ± 102



**Fig. 5** Water saturation level at different temperatures

last 4 points) of water readings after stabilisation were used to calculate the saturation level. The stabilised values of each temperature are given in Table 2.

After calculating the saturation levels at 80, 60, 40 and 20 °C, the saturation points were used to draw the water saturation curve at different temperatures as plotted in Fig. 5.

The results exhibit that dissolved water content in the engine oil increases with an increase in temperature (Fig. 5). This confirms that as the temperature of engine oil decreases, free water is separated into the oil. Regardless of the saturation level of the oil, the saturation curve provides a true

indication of the risk when the free water starts to exist in the engine oil. The higher temperature of engine oil, it can hold more dissolved water compared to lower temperature oil [6]. This phenomenon is because heating increases kinetic energy among water molecules, causing them to break apart and facilitating the entry of more dissolved water into the oil [28].

### 2.2 Tribological Tests

TE77 tribometer was used to imitate the reciprocating motion conditions in the engine according to ASTM G 181 [33]. The material properties of the pin and plate and experimental test conditions are determined in Table 3. In these test conditions, the Lambda is  $\lambda = 0.27 < 1$  which refers to boundary lubrication regime. The Hertzian contact equation was used to calculate the maximum contact pressure ( $P_{max}$ ). The test temperature was selected at 100 °C to replicate the working conditions in a real engine.

### 2.3 Post surface Analysis

The wear volume loss on the pin surface after tribological test was measured by an optical white light interferometer (NPFLEX, Bruker, USA). The Vision64 programme from Bruker corporation has been used to analyse the wear scar of pins after NPFLEX measurement. The volume loss on the pin surface, which is similar to a spherical cap, is calculated using Eqs. (3) and (4) as follows:

$$V_{pin \text{ volume loss}} = \frac{\pi \cdot h^2 \cdot (3R - h)}{3} \tag{3}$$

$$h = R - (R^2 - r^2)^{0.5} \tag{4}$$

$r$  wear scar radius ( $\mu\text{m}$ ),  $R$  sphere radius ( $\mu\text{m}$ ),  $h$  spherical cap height ( $\mu\text{m}$ ).

Atomic force microscopy (AFM, Bruker, USA) was used as an imaging technique in this paper to measure the surface topography of the sample surface with a picometer high resolution. AFM cantilever was used with a nominal spring constant of 40 N/m and a resonant frequency of 2 kHz. High-resolution AFM images with an area size of  $10 \times 10$

**Table 3** Materials properties of contact surfaces and TE77 tribometer test conditions

Material properties	Pin	Plate	TE77 parameters	Value
Material	Steel EN31	Steel EN31	Temperature °C	100
Dimensions (mm)	10 radius	7*7*3	Contact pressure (GPa)	0.92
Hardness (HRC)	58–62	58–62	Load (N)	28
roughness (nm)	30–50	400–600	Frequency (Hz)	25
Elastic modulus (GPa)	190–210	190–210		
Poisson’s ratio	0.28	0.28	Test duration (mins)	120

$\mu\text{m}^2$  were captured. The AFM tip was centred in the wear scar of the pin surface. The images were captured at a low contact force of 45 nN and a speed of 40  $\mu\text{m}/\text{s}$ . The scanning angle during the imaging was fixed at an angle of 90°.

After the friction test, elemental analysis of the surface layer was carried out using X-ray Photoelectron Spectroscopy (XPS) (Harwell XPS, UK). Before the XPS analysis, all samples were cleaned with heptane to remove the oil from the wear scar. The XPS spot of 200  $\mu\text{m} \times 100 \mu\text{m}$  was centred in the middle of the wear scar. The XPS was run at an X-ray source energy of 1486.69 eV, an X-ray strength of 19.2 W, an Iron gun current of 150  $\mu\text{A}$  and a voltage of 45 V. The temperature and pressure during XPS analysis were 294 K and below  $10^{-8}$  Torr respectively. The spectra of samples were analysed using CaseXPS software. The deconvolution of XPS signals was performed by fitting them with the peaks using the line shape of the Gaussian/Lorentzian (GL) formula. The fitted peaks were correlated to the available literature [23, 29, 34–37].

### 3 Results and Discussion

#### 3.1 Additives Depletion by Water

The results (Fig. 5) showed that the water saturation level is correlated to the oil temperature. The change in oil temperature over time causes a separation of free water, which settles down in the bottom of the glass bottle. Free water could affect the concentration of the additive due to the high polarity of water molecules [9]. Additives can be depleted when the free water separates from the oil. To study the effect of separation of different levels of free water on additives depletion, the oil was aged with different levels of 0.3, 0.5, and 1 wt% of water for 48 h and at a stirring speed of 500 rpm at a temperature of 80 °C. Ageing parameters were chosen to ensure that water molecules in oils can interact with additives sufficiently [13, 14]. The test bottle was filled with oil containing different water levels and sealed to avoid the evaporation of water during the ageing process. The mixing of water in the oil at different levels guarantees consistent test conditions, enough amount of oil for the tribological test and further chemical analysis, producing the aged oil containing water for the following tests in a short period compared to the water saturation method presented in this paper. The oils, after ageing, were centrifuged for 2 h to remove the free water from the oil. Water content before and after centrifugation was determined by KF, as shown in Table 4.

ICP analysis was conducted on oil samples after centrifugation to determine the change in the additive concentration, as presented in Fig. 6. The results generally demonstrated a reduction in additive elements concentration, after removing

**Table 4** Water content in oils as measured by KF before and after centrifugation

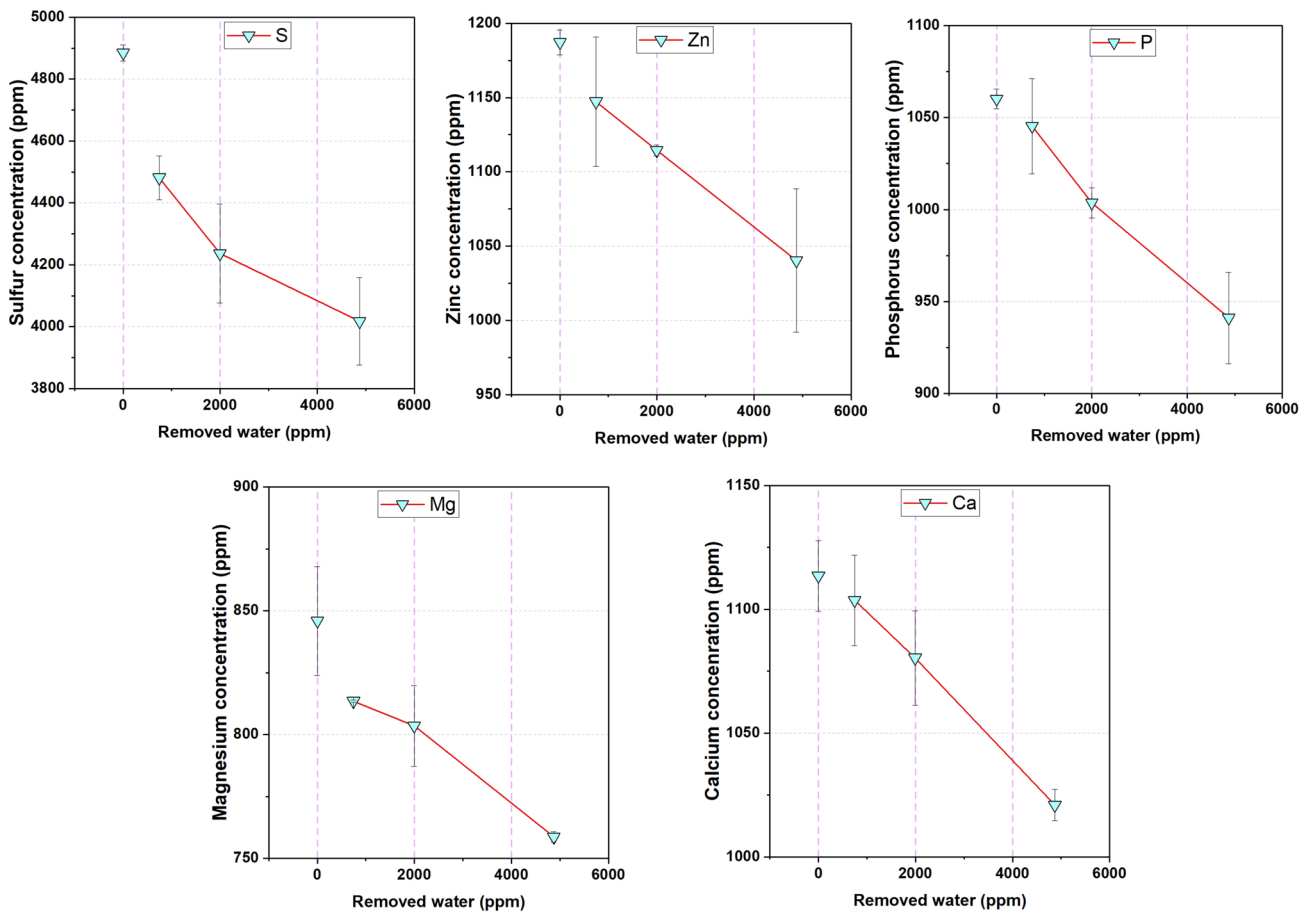
Details	Added water		
	0.3%	0.5%	1%
Water in oil (ppm)	3828	6268	11,875
Water after 48h ageing (ppm)	2790	4648	7509
Water after centrifuge (ppm)	2045	2651	2637

the free water compared to fresh oil (the first reading point is used as the reference point). The S, P, Zn, Ca and Mg concentrations decrease with increased amount of removed water. The results proved that additives depletion by water occurred after removing the water from the oil. The reduction of S, P and Zn, as demonstrated in Fig. 6, comes from the depletion of antiwear additives (ZDDP). Meanwhile, S and P could also originate from dispersants/detergents such as sulfonates and phosphonates [27]. The reduction in Mg and Ca concentration originates from depletion in detergents/dispersants such as magnesium or calcium sulfonates [38].

The result can be described as water-polar molecules with additives producing reverse micelles. The heads of additives latch easily onto water molecules and surround them, as illustrated in Fig. 7 [9]. When the water content in oil exceeds the saturation level, water molecules surrounded by additives separate from the oil, causing the depletion of additives. The results align with the function of dispersants/detergents where more polar groups capture or attach to the organic contaminants. It is expected to be removed by water, as illustrated in Fig. 7 [2, 18]. The results exhibit the effect of a change in water level on additives depletion after reaching saturation level, as demonstrated in Fig. 7. As more water separates from oil above the saturation level, more additives are depleted. The reduction in additive concentration could affect engine oil performance. Table 4 displays that the remaining dissolved water is above 2,000 ppm after centrifugation, which could influence wear. Post-investigations have been conducted to understand the effect of additives depletion and remaining water on wear.

#### 3.2 Water Effect on Oil Degradation

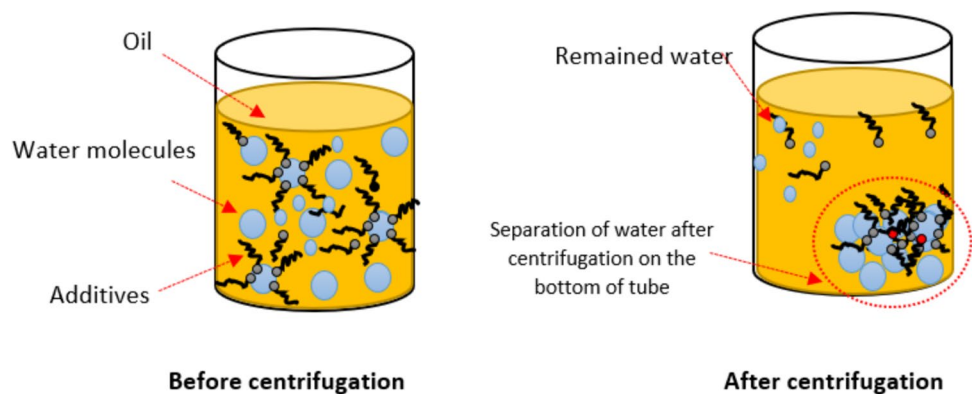
FTIR data of bulk oils after removing the free water from the aged oil by centrifugation are plotted in Fig. 8a. The P – O – C region at 978  $\text{cm}^{-1}$  which indicates the presence of ZDDP antiwear additives are displayed in Fig. 8b [39]. The sulfate by-products in FTIR spectra can be determined in regions around 1,150 and 1,250  $\text{cm}^{-1}$  [20, 40]. FTIR spectra can also identify the oil oxidation (C = O) in region at 1,720  $\text{cm}^{-1}$  are shown in Fig. 8c [39]. The results indicate that the anti-wear additive at the 978  $\text{cm}^{-1}$



**Fig. 6** Elemental concentration (S, Zn, P, Mg and Ca) of additive of aged oil samples after removing free water. Four oil samples were used, including fresh oil, aged oil + 0.3 wt% water-after centrifuge,

aged oil + 0.5 wt% water-after centrifuge, and aged oil + 1 wt% water-after centrifuge

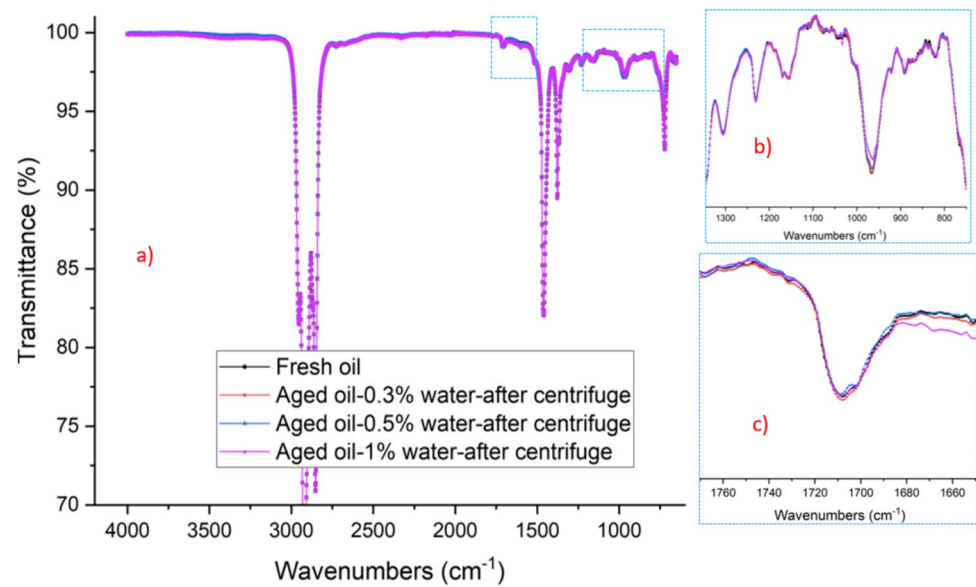
**Fig. 7** Schematic images explain the principle of additives depletion by water



region decreased slightly. The chemical analysis of oils demonstrates no degradation products (such as oxidation or sulfation products) caused by water under ageing conditions (Fig. 8b, c). Other studies [13, 14] suggested that ZDDP decomposition occurred or was accelerated not only

by thermal decomposition but also due to the hydrolysis process during the rubbing of metal surfaces. The previous studies [13, 14] suggested that water can destroy ZDDP antiwear additive when it reacts with water at a temperature of 60 °C and above during the tribology test.

**Fig. 8** FTIR chemical analysis of aged oils with different levels of water-after removing the free water from oil samples; water level before and after centrifugation was measured by KF as shown in Table 4 (a). The P – O – C and sulfate by-products regions in FTIR spectra (b). The oil oxidation region at  $1720\text{ cm}^{-1}$  (c)



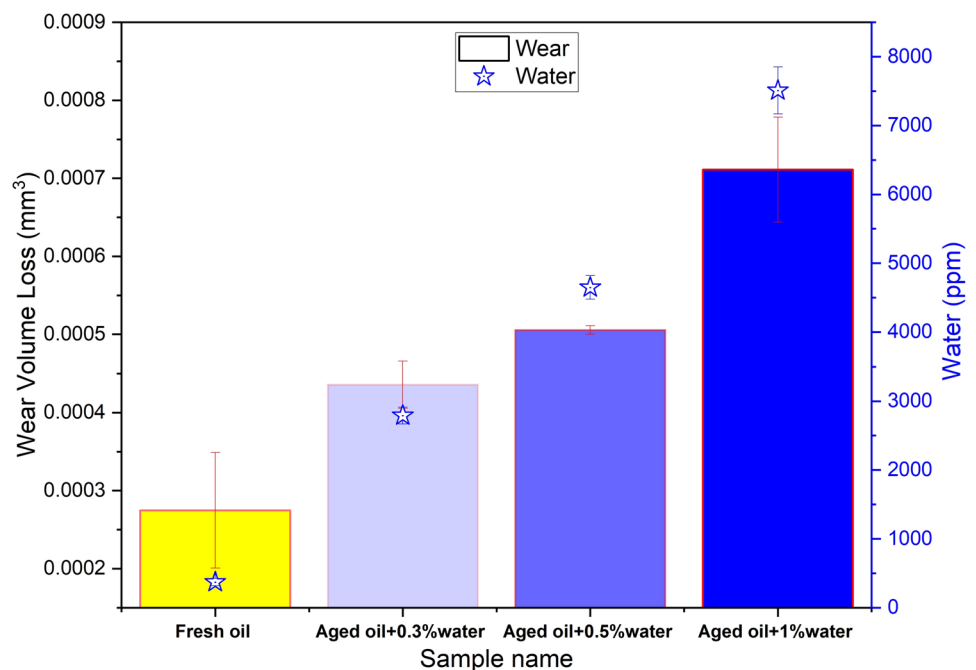
### 3.3 Water Effect on Wear

Tribological tests were performed using the TE77 tribometer for aged oils containing water. TE77 working conditions are demonstrated in Table 3. The tribological tests were run before and after removing the water from the oil. Based on the wear results shown in Fig. 9, it can be observed that wear increases with an increase in water content in the oil, as expected. The results align well with other studies [21–23] that stated that water contamination significantly affects wear and tribofilm formation. Water contamination

influenced the formation and growth of tribofilm producing higher wear [41]. Fitch et al. [42] showed that an antiwear additive, which forms tribofilm at a high temperature, can be destroyed even by a slight amount of water in the oil.

According to saturation tests, the water level was changed depending on the oil temperature by releasing free water at a lower temperature. Water separation from the oil caused additives depletion, as shown in Fig. 6. Water level after centrifugation was measured by KF, and the results show that the remaining water in oils (which is less than 2,500 ppm) represents the dissolved water in oil samples. To investigate

**Fig. 9** Wear after ageing the oil with different levels of water (before centrifuge)





whether additives depletion and remaining water influence the wear rate, wear tests were conducted after removing the free water from aged oil. Figure 10 shows a slight increase in wear with an increase in removed water from oil due to additives depletion. When the dissolved water is present in the oil, hydrolysis of polyphosphates occurs, resulting in the formation of short-chain polyphosphates causing higher wear [41]. Chemical analysis of the tribofilm will result in gaining insights into the real mechanism involved in the post-analysis in this study.

### 3.4 Water Effect on Tribofilm Topography

Topography features of tribofilm were characterised using the AFM technique. Wear results demonstrated an increase in wear with the increase in the level of the water as displayed in Fig. 9. The presence of water in oils accelerates the decomposition of antiwear additives and the formation of shorter polyphosphate chains in tribofilm [14]. Tribofilm formation was influenced by water according to previous studies [22, 23] in terms of thickness of tribofilm and coverage or uniformity of antiwear film on the metal surface. Figure 11b–d show AFM images of tribofilm on the wear scar of pins for oils containing different levels of water. The images show a distribution or tribofilm pits in the surface (distribution of dark spots) in the existence of water compared to the tribofilm of fresh oil displayed in Fig. 11a. Water level influences the uniformity of tribofilm and more pits can be observed with an increase in the water content.

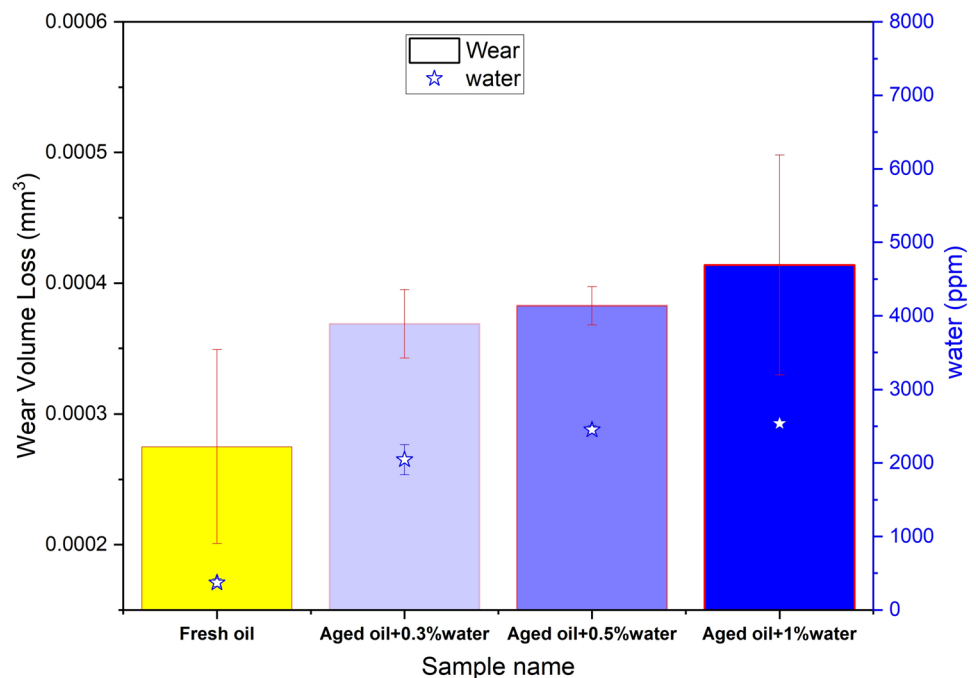
Oils after removing the water influence the oil performance causing an increase in wear as shown in Fig. 10.

AFM images (Fig. 11b1, c1 and d1) of oil samples after centrifugation reveal less effect on tribofilm. There is still discontinuity or pits in the tribofilm due to additives depletion and remaining dissolved water. The growth rate and morphology of these films, which are formed on steel substrates, are distinguishable and influenced by dissolved water and additives depletion.

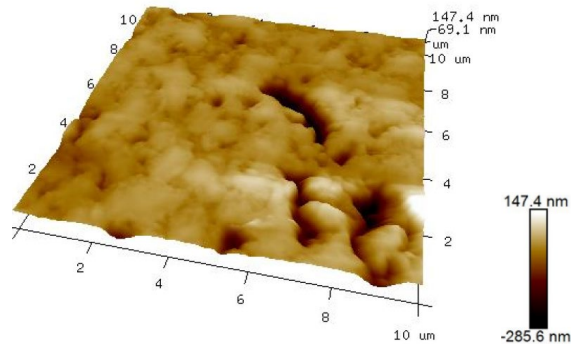
### 3.5 Water Effect on Tribofilm Chemistry

The surface chemistry of tribofilm mainly consists of zinc polyphosphate chains [29]. Zinc polyphosphates in the tribofilm can be determined using the XPS technique [29, 34, 35]. The oxygen 1s signal from XPS data were fitted by two peaks bridging (P–O–P) and non-bridging oxygen (P=O and P–O–M, with M being a metal) [34, 35]. It has been proved that the chain length of zinc polyphosphates can be characterised based on the intensity ratio of the bridging oxygen/non-bridging oxygen (BO/NBO) and the binding energy difference between  $Zn3s-P2p_{3/2}$  [34, 43]. This combined method is applied to characterise the polyphosphate chain ranging from zinc orthophosphate to zinc metaphosphate depending on BO/NBO values [34, 43]. Crobu et al. [34, 44] assessed the length of polyphosphate chains depending on the (BO/NBO) values. If the BO/NBO values are less than 0.2, short chains of polyphosphate, which are called orthophosphate chains, will be formed. If BO/NBO values are bigger than 0.37, the long chains of polyphosphate, which are called metaphosphate chains, will be found in the tribofilm.

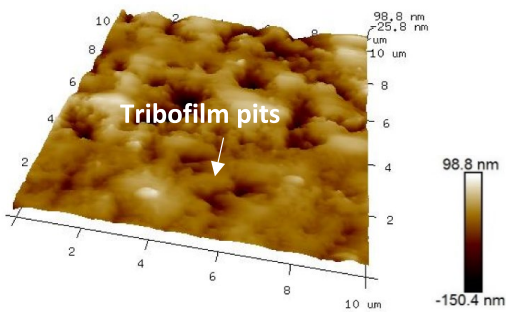
**Fig. 10** Wear volume loss after removing the free water from oils by centrifugation



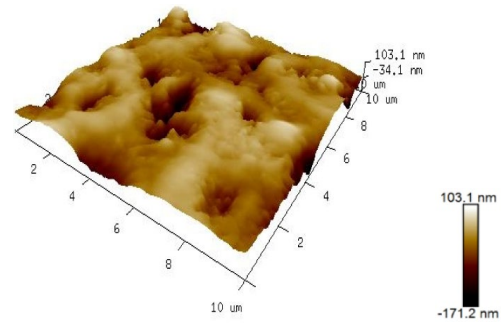
a) Fresh oil



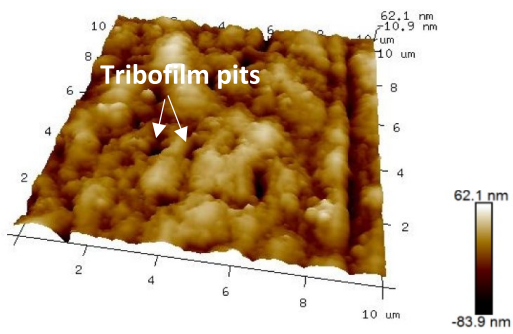
b) Aged oil+0.3%water



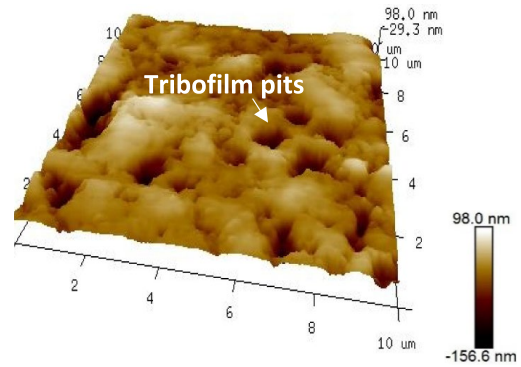
b<sub>1</sub>) Aged oil+0.3%water-after centrifuge



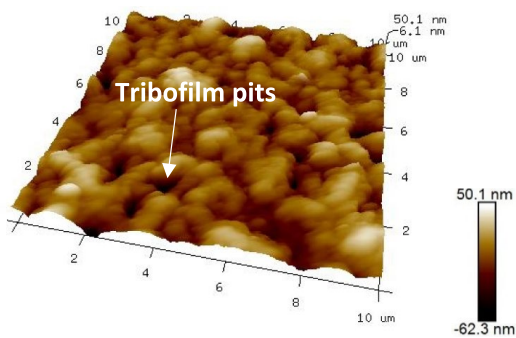
c) Aged oil+0.5%water



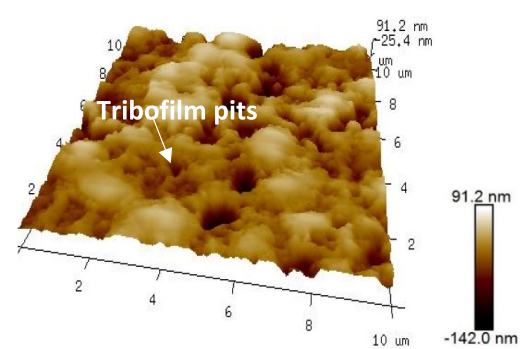
c<sub>1</sub>) Aged oil+0.5%water-after centrifuge



d) Aged oil+1%water



d<sub>1</sub>) Aged oil+1%water-after centrifuge



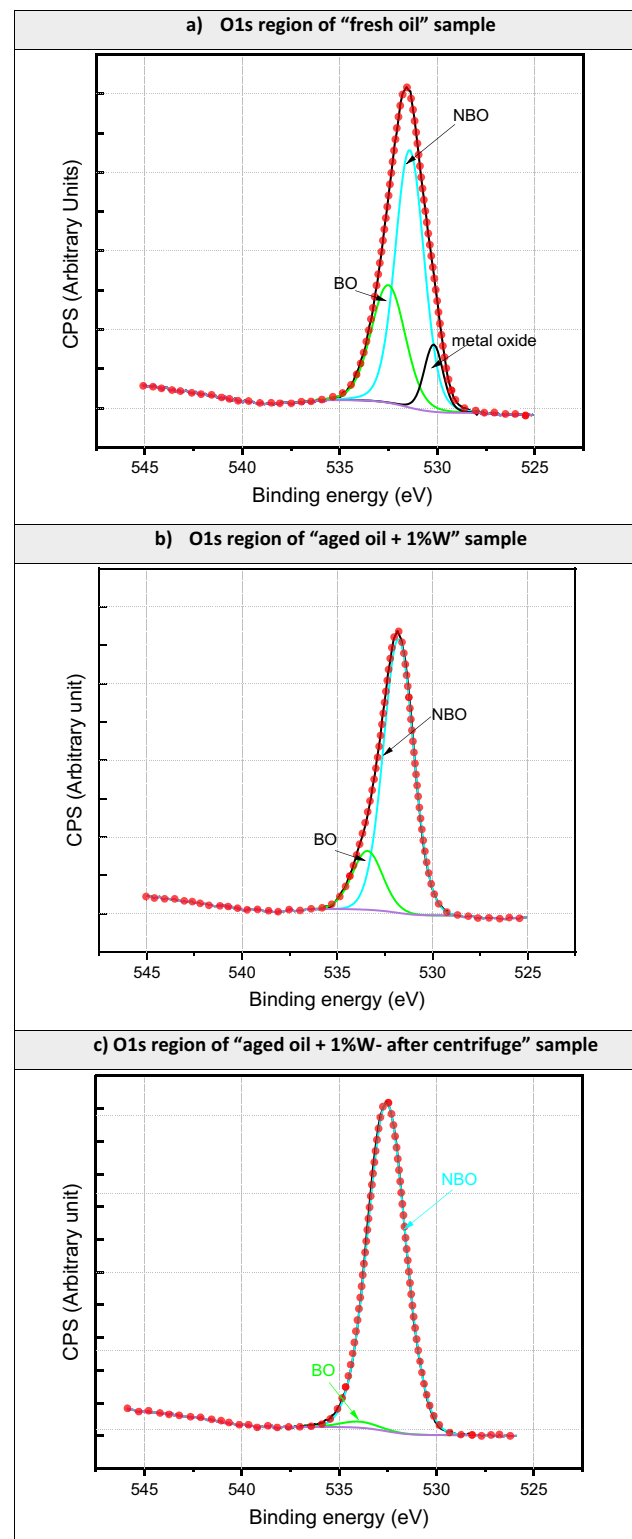
**Fig. 11** AFM images of tribofilm formed on pin surface; **a** fresh oil, **b** aged oil + 0.3 wt% water, **c** aged oil + 0.5 wt% water, **d** aged oil + 1 wt% water. AFM images of the oils samples after centrifuging the free water; **b1** aged oil + 0.3 wt% water, **c1** aged oil + 0.5 wt% water, **d1** aged oil + 1 wt% water

In this study, the chemistry of tribofilm on pins for all aged oils tests was conducted using XPS analysis. The oxygen 1s peaks from XPS data were plotted and fitted by BO and NBO peaks, as shown in Fig. 12a–c. The results show that fresh oil is responsible for the longest polyphosphate chains and metal oxide [34, 43] was found on the surface as demonstrated in Fig. 12a. Figures 13 and 14 demonstrate the results for BO/NBO and the binding energy difference between Zn3s–P2p<sub>3/2</sub> at different levels of water and after removing the free water from oils. It can be noted that BO/NBO values decrease and Zn3s–P2p<sub>3/2</sub> values increase in the presence of water. Figure 12b reveals that the presence of water in oil affects the length of polyphosphate chains forming short chains. This can be interpreted as the presence of water causing the formation of shorter orthophosphate chains. The length of orthophosphate chains can be affected by the water percentage presented in the oil as shown in Fig. 13. The results are in line with studies in terms of the formation of short orthophosphate chains in the presence of water [23, 36]. It also supports the fact that a higher concentration of water in the oil could also influence the length of glassy phosphate chains [41].

The chemistry of tribofilm of tests after removing the free water by centrifugation was analysed. Based on the BO/NBO ratios represented in Fig. 14, the results indicate that dissolved water and additives depletion by water can also affect the length of polyphosphate chains. Figure 12c reveals that the intensity of the BO peak decreases after removing the water due to the removal of P–O–P compounds (BO bridge). Figure 14 shows a decrease in BO/NBO values and an increase in Zn3s–P2p<sub>3/2</sub> values which refer to the formation of short polyphosphate chains.

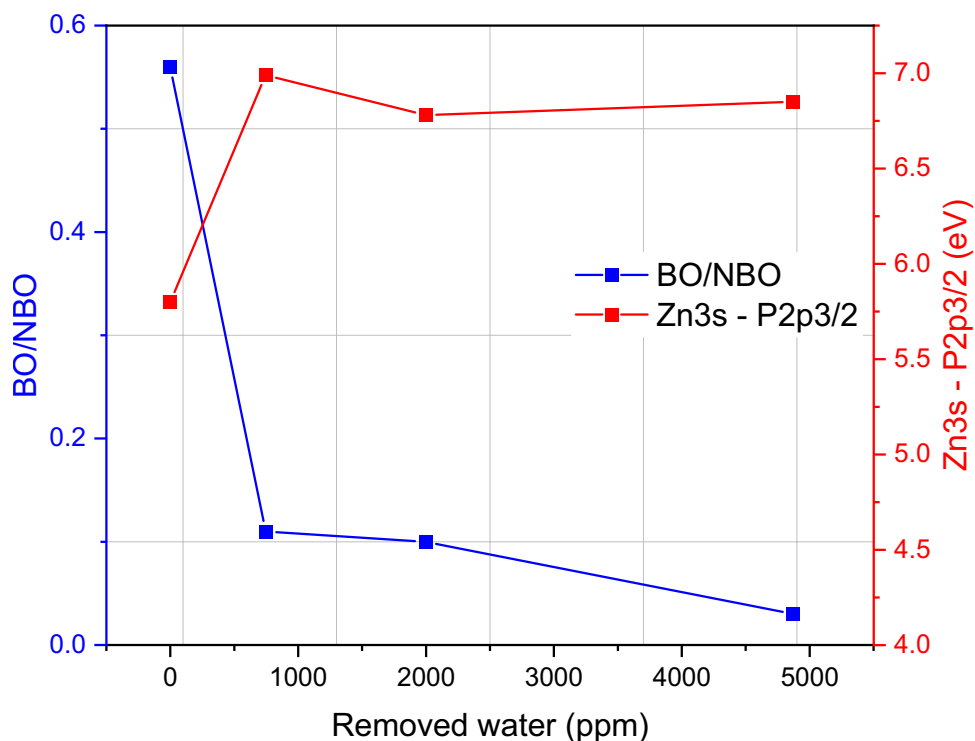
The results are in line with other studies [15, 45] which claimed that the chain polyphosphates can be depolymerised by water to shorter chains. Equations (1) and (2) describe the mechanisms of depolymerisation of polyphosphate chains in the existence of water. The hydrolysis of polyphosphates in the presence of water occurs producing short-chain polyphosphates.

The XPS results of wear scar of pins were quantified before and after removing free water from aged oil samples as shown in Table 5. The chemistry of tribofilm for oil samples was compared to fresh oil sample. The XPS results (Table 5) demonstrate a significant decrease in the elemental concentration of tribofilm such as sulphur, zinc and phosphorus in the existence of free water in the oil (before centrifugation). After centrifugation (after removing free

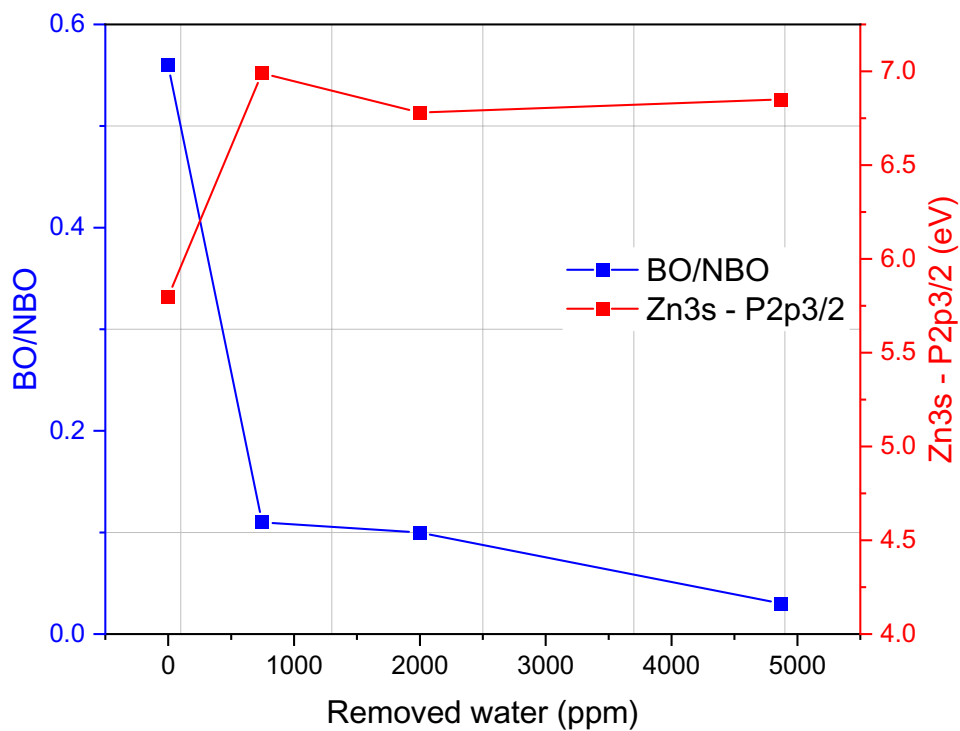


**Fig. 12** XPS oxygen 1s spectra from pins surface for oil samples **a** fresh oil, **b** aged oil + 1% water, **c** aged oil + 1% water-after centrifuge

**Fig. 13** Water concentration effect on polyphosphate chain length



**Fig. 14** Effect of the remaining water and additives depletion on the length of polyphosphate chains



water), the XPS analysis of tribofilm shows also decrease in the concentration of tribofilm elements (sulphur, zinc and

phosphorus) due to remaining dissolved water and additives depletion.

**Table 5** XPS quantification of wear scar of pins to quantify the chemistry of tribofilm before and after centrifuge

Sample details	XPS quantification (At %)					
	Carbon (C 1s)	Iron (Fe 2p)	Oxygen (O 1s)	Sulphur (S 2p)	Zinc (Zn 2p)	Phosphorus (P 2p)
Fresh oil	20.92	6.69	49.18	2.02	15.41	5.77
Aged oil + 0.3 wt% water	30.98	5.76	45.49	2.31	12.08	3.38
Aged oil + 0.5 wt% water	37.31	2.4	47.52	1.28	7.9	3.59
Aged oil + 1 wt% water	21.38	13.98	51.81	1.29	8.73	2.81
Aged oil + 0.3 wt% water-after centrifuge	26.13	10.05	46.86	1.56	11.5	3.91
Aged oil + 0.5 wt% water-after centrifuge	22.61	11.53	50.64	1.89	9.7	3.62
Aged oil + 1 wt% water-after centrifuge	24.61	9.63	49.45	1.76	10.73	3.84

## 4 Conclusions

In this study, the effect of water contamination on oil performance and its additives have been investigated. This study determined the water saturation level in the lubricant for first time. The water level in oils is unstable and changes from one phase to another causing the separation of free water in the oil. This influence oil performance and its additives. The key findings are summarised as follows:

- The results showed the ability of the oil to hold more dissolved water at a higher temperature.
- Removal of free water from the oil resulted in additives depletion.
- Wear was increased after removing free water from the oils due to additives depletion.
- Tribofilm topography of contact surface for oils containing dissolved or free water showed the discontinuity of antiwear film on the contact surface.
- The hydrolysis of polyphosphates in the presence of dissolved or free water occurred producing short-chain polyphosphates.

**Acknowledgements** The authors would like to thank Parker Hannifin and the EPSRC Centre for Doctoral Training for Integrated Tribology for providing funding for this research (Grant No. EP/I01629X/1).

**Author Contributions** A. Al Sheikh Omar: conceptualization, methodology, investigation, analysis, writing and reviewing of the original draft. F. Motamen Salehi: conceptualization, methodology, investigation, analysis, editing and reviewing of the manuscript. A. Morina: conceptualization, methodology, investigation, analysis, editing and reviewing of the manuscript. U. Farooq: labs materials, conceptualization, methodology, investigation and analysis.

**Data Availability** The data supporting this study are openly available whenever requested.

## Declarations

**Competing interests** The authors declare no competing interests.

**Open Access** This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons licence, and indicate if changes were made. The images or other third party material in this article are included in the article's Creative Commons licence, unless indicated otherwise in a credit line to the material. If material is not included in the article's Creative Commons licence and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this licence, visit <http://creativecommons.org/licenses/by/4.0/>.

## References

1. George, S., Balla, S., Gautam, V., Gautam, M.: Effect of diesel soot on lubricant oil viscosity. *Tribol. Int.* **40**(5), 809–818 (2007). <https://doi.org/10.1016/j.triboint.2006.08.002>
2. Evans, J.: How do oils degrade? *Wear Check* **52**, 1–6 (2011)
3. Raymond, L.: *Hydrogen Embrittlement: Prevention and Control*, vol. 962. ASTM International, West Conshohocken (1988)
4. Ray, G., Fogel, G.: Estimating water content in oils: moisture in solution, emulsified water, and free water. In: *Proceedings of a Joint Conference Technology Showcase: Integrated Monitoring, Diagnostics and Failure Prevention*. (1996)
5. Harika, E., Bouyer, J., Fillon, M.: Impact of lubricant contamination with water on hydrodynamic thrust bearing performance. *Mech. Ind.* **12**, 553 (2010)
6. Pall, M. D., Vesala, M.: Setting control limits for water contamination in hydraulic and lube systems. In: *The 10th Scandinavian International Conference on Fluid Powe*, pp. 1–7. (2009)
7. Peter Clark, J.: Emulsion: when oil and water do mix. *Food Technol.* **67**(8), 1–8 (2013)
8. Leigh-Jones, C.: Water contamination in oil. *Motor Ship* **85**(1005), 34–35 (2004)
9. Smiechowski, M. F., Martin, H. B.: electrochemical characterization of lubricants for microfabricated sensor applications. PhD Thesis. (2005)
10. Cantley, R.E.: The effect of water in lubricating oil on bearing fatigue life. *ASLE Trans.* **20**(3), 244–248 (1977). <https://doi.org/10.1080/05698197708982838>
11. Needelman, W., LaVallee, G.: Forms of water in oil and their control. In: *Noria Lubrication Excellence Conference*, Columbus Ohio. (2006)

12. Ave, B., Worth, F.: Water contamination: management of water during the lubricant life cycle. (2009)
13. Spedding, H., Watkins, R.C.: The antiwear mechanism of zddp's. Part I. *Tribol. Int.* **15**(1), 9–12 (1982)
14. Rounds, F.G.: Some factors affecting the decomposition of three commercial zinc organodithiophosphates. *ASLE Trans.* **18**(2), 79–89 (1975)
15. Fuller, M.S., Kasrai, M., Bancroft, G., Fyfe, K., Tan, K.H.: Solution decomposition of zinc dialkyl dithiophosphate and its effect on antiwear and thermal film formation studied by X-ray absorption spectroscopy. *Tribol. Int.* **31**, 627–644 (1998)
16. Sander, J.: Water Contamination: Management of Water During the Lubricant Life Cycle, pp. 1–9. Lubrication Engineers Inc., Fort Worth (TX) (2009)
17. Bagi, S., Sharma, V., Patel, M., Aswath, P.B.: Effects of diesel soot composition and accumulated vehicle mileage on soot oxidation characteristics. *Energy Fuels* **30**(10), 8479–8490 (2016). <https://doi.org/10.1021/acs.energyfuels.6b01304>
18. Minami, I.: Molecular science of lubricant additives. *Appl. Sci.* **7**, 445 (2017). <https://doi.org/10.3390/app7050445>
19. Lancaster, J.K.: A review of the influence of environmental humidity and water on friction, lubrication and wear. *Tribol. Int.* **23**(6), 371–389 (1990). [https://doi.org/10.1016/0301-679X\(90\)90053-R](https://doi.org/10.1016/0301-679X(90)90053-R)
20. Penchaliah, R., Harvey, T.J., Wood, R.J.K., Nelson, K., Powrie, H.E.G.: The effects of diesel contaminants on tribological performance on sliding steel on steel contacts. *Proc. Inst. Mech. Eng. Part J* **225**(8), 779–797 (2011). <https://doi.org/10.1177/1350650111409825>
21. Parsaeian, P., Van Eijk, M.C.P., Nedelcu, I., Neville, A., Morina, A.: Study of the interfacial mechanism of ZDDP tribofilm in humid environment and its effect on tribochemical wear; Part I: Experimental. *Tribol. Int.* **107**, 135–143 (2017). <https://doi.org/10.1016/j.triboint.2016.11.012>
22. Parsaeian, P., et al.: An experimental and analytical study of the effect of water and its tribochemistry on the tribocorrosive wear of boundary lubricated systems with ZDDP-containing oil. *Wear* **358–359**, 23–31 (2016). <https://doi.org/10.1016/j.wear.2016.03.017>
23. Cen, H., Morina, A., Neville, A., Pasaribu, R., Nedelcu, I.: Effect of water on ZDDP anti-wear performance and related tribochemistry in lubricated steel/steel pure sliding contacts. *Tribol. Int.* **56**, 47–57 (2012). <https://doi.org/10.1016/j.triboint.2012.06.011>
24. Costa, H.L., Spikes, H.A.: Impact of ethanol on the formation of antiwear tribofilms from engine lubricants. *Tribol. Int.* **93**, 364–376 (2016). <https://doi.org/10.1016/j.triboint.2015.09.021>
25. Dorgham, A., Azam, A., Parsaeian, P., Wang, C., Morina, A., Neville, A.: An assessment of the effect of relative humidity on the decomposition of the ZDDP antiwear additive. *Tribol. Lett.* **69**(2), 1–12 (2021). <https://doi.org/10.1007/s11249-021-01446-6>
26. ASTM: D5185, Standard test method for multielement determination of used and unused lubricating oils and base oils by inductively coupled plasma atomic emission spectrometry (ICP-AES). Annual Book of Standards. (2013)
27. Lubrecht, A.A., Venner, C.H., Colin, F.: Film thickness calculation in elasto-hydrodynamic lubricated line and elliptical contacts. *Proc. Inst. Mech. Eng. Part J* **223**(3), 511–515 (2009)
28. Qin, Y., Wu, Y., Liu, P., Zhao, F., Yuan, Z.: Experimental studies on effects of temperature on oil and water relative permeability in heavy-oil reservoirs. *Sci. Rep.* **8**(1), 1–9 (2018). <https://doi.org/10.1038/s41598-018-31044-x>
29. Crobu, M., Rossi, A., Mangolini, F.: Chain-length-identification strategy in zinc polyphosphate glasses by means of XPS and ToF-SIMS. *Anal. Bioanal. Chem.* **403**(5), 1415–1432 (2012)
30. ASTM: Designation: D 6304-04 e1: Standard test method for determination of water in petroleum products, lubricating oils, and additives by Coulometric Karl Fischer Titration 1. [www.astm.org](http://www.astm.org)
31. Nguele, R., Al-salim, H.S., Mohammad, K.: Modeling and forecasting of depletion of additives in car engine oils using attenuated total reflectance fast transform infrared spectroscopy. *Lubricants* **21**, 206–222 (2014). <https://doi.org/10.3390/lubricants2040206>
32. Superseding, I. R., et al.: Vehicle recommended. (2018)
33. Truhan, J.J., Qu, J., Blau, P.J.: A rig test to measure friction and wear of heavy duty diesel engine piston rings and cylinder liners using realistic lubricants. *Tribol. Int.* **38**(3), 211–218 (2005)
34. Crobu, M., Rossi, A., Mangolini, F., Spencer, N.D.: Tribochemistry of bulk zinc metaphosphate glasses. *Tribol. Lett.* **39**(2), 121–134 (2010). <https://doi.org/10.1007/s11249-010-9622-4>
35. Zhang, J., Ueda, M., Campen, S., Spikes, H.: Boundary friction of ZDDP tribofilms. *Tribol. Lett.* **69**(1), 1–17 (2021). <https://doi.org/10.1007/s11249-020-01389-4>
36. Nedelcu, I., Piras, E., Rossi, A.: XPS analysis on the influence of water on the evolution of zinc dialkyldithiophosphate-derived reaction layer in lubricated rolling contacts. *Surf. Interface Anal.* **44**(8), 1219–1224 (2012)
37. Heuberger, R., Rossi, A., Spencer, N.D.: XPS study of the influence of temperature on ZnDTP tribofilm composition. *Tribol. Lett.* **25**(3), 185–196 (2007). <https://doi.org/10.1007/s11249-006-9166-9>
38. Fialkovskii, A.B., Korbut, R.V., Lisovskaya, L.F., Vipper, M.A.: Magnesium sulfonate additives. *Chem. Technol. Fuels Oils* **19**(3), 31–32 (1983)
39. Hernández-Sierra, M.T., Aguilera-Camacho, L.D., Báez-García, J.E., García-Miranda, J.S., Moreno, K.J.: Thermal stability and lubrication properties of biodegradable castor oil on AISI 4140 steel. *Metals* **8**(6), 428 (2018). <https://doi.org/10.3390/met8060428>
40. Dörr, N., Agocs, A., Besser, C., Ristić, A., Frauscher, M.: Engine oils in the field: a comprehensive chemical assessment of engine oil degradation in a passenger car. *Tribol. Lett.* (2019). <https://doi.org/10.1007/s11249-019-1182-7>
41. Parsaeian, P., Van Eijk, M.C.P., Nedelcu, I., Neville, A., Morina, A.: Tribology International Study of the interfacial mechanism of ZDDP tribofilm in humid environment and its effect on tribochemical wear; Part I: Experimental. *Tribol. Int.* **107**, 135–143 (2017). <https://doi.org/10.1016/j.triboint.2016.11.012>
42. Fitch, J.C., Jaggernauth, S.: Moisture—the second most destructive lubricant contaminate, and its effects on bearing life. *P/PM Technol.* **12**(5), 1–4 (1994)
43. Liu, E., Kouame, S.D.: An XPS study on the composition of zinc dialkyl dithiophosphate tribofilms and their effect on camshaft lobe wear. *Tribol. Trans.* **57**(1), 18–27 (2013). <https://doi.org/10.1080/10402004.2013.835014>
44. Crobu, M., Rossi, A., Mangolini, F., Spencer, N.D.: Chain-length-identification strategy in zinc polyphosphate glasses by means of XPS and ToF-SIMS. *Anal. Bioanal. Chem.* **403**(5), 1415–1432 (2012). <https://doi.org/10.1007/s00216-012-5836-7>
45. Nicholls, M., Do, T., Norton, P., Kasrai, M., Bancroft, G.: Review of the lubrication of metallic surfaces by zinc dialkyl-dithiophosphates. *Tribol. Int.* **38**, 15–39 (2005). <https://doi.org/10.1016/j.triboint.2004.05.009>

**Publisher's Note** Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.