

Impact of biodegradable lubricant oils on soil element concentrations

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Abstract. This study deals with the biodegradation of vegetable oils commonly used in the forestry industry. Sampling was performed in the National nature reserve Slnčné skaly in Rajecká basin, Slovakia. Eighty soil samples contaminated with biodegradable lubricant oil and eighty control samples were collected. The samples were collected from ten pairs of plots (oil and control) once a week for eight calendar weeks following chain saw use. Biodegradable vegetable oil had significant effects on the concentration of several elements. Amounts of K, Ti, Mn, Cr, Fe, Rb, Sr, Zr and Ba significantly decreased in some of the oil plots when compared to control plots. However, this effect was found to be related to the unique environmental conditions of these plots. Element concentrations in soil samples were observed to be reduced approximately three weeks following the commencement of the experiment, corresponding to the estimated time of degradation of our used oil. The biodegradable oil had a negative effect on Ca binding in the soil and this study found that oil tends to have an effect on the binding of Ca in the soil after 5 weeks. The oil samples had higher levels of Pb and S than the control samples, whereas the contents of S and Pb were closely related. Sulphur likely decreased soil pH and increased availability and mobility of Pb. Additionally, the biodegradable lubricant oil had a slight non-significant negative impact on amounts of Cu found in the soil.

Key words: environmental pollution, ecotoxicity, oils, biodegradability, soils, heavy metals

Introduction

Forestry machinery used on forest roads and in forest areas presents an ecological threat due to pollution caused by the leakage of lubricant oil and other petroleum products (Stanovský *et al.* 2013). Recently, effort has been put into developing environmen-

tally friendly lubricants, which are biodegradable or of biological origin. From an environmental point of view, however, the utilization of recycled synthetic or mineral oils has a negative effect on the soil and water in these ecosystems (Stanovský *et al.* 2013; Nowak *et al.* 2019). Oils produced from crude oil (mineral oils) cause serious contamination of soils, groundwater, and can accumulate in plant tissues (Nowak *et al.* 2019). Forestry workers avoid bio-oils because their lubricating characteristics are not as good as those of conventional lubricants are much more expensive. Bio-oil does not provide better lubrication for chainsaws and in some cases, it performs worse than used synthetic motor oil (Skoupý 2004). However, vegetable oil-based lubricants biodegrade much more quickly compared to mineral-oil based or synthetic lubricants (Erhan and Asadauskas 2000; Haigh 1995).

The biodegradability means the tendency of a lubricant to be ingested and metabolized by microorganisms. Complete biodegradability indicates that the lubricant has essentially returned to nature (Bartz 1998). Biodegradability varies depending on the type of oil, and the presence of toxic compounds affecting microorganisms plays a part in this process. Toxic compounds in mineral oils could include metals, degradation products like acrolein, peroxides or polymers. Sometimes vegetable oil contains aldehydic compounds, as a consequence of thermal degradation (Cecutti and Agius 2008). Vegetable or natural oils are triglycerides of natural fatty acids, palmitic acid, stearic acid, oleic acid, vegetable oils, linolenic acid, etc. One of the most important natural oils is rape seed oil. Due to its high content of unsaturated fatty acids, natural oils tend to have low oxidation stability (Bartz 1998). According to Lauhanen *et al.* (2000), the degradability of rape seed oil is faster than that of mineral oils in the field. Biodegradability of lubricants varies; from 21 to 24 days after use for bio-oils, 35 to 40 days for mineral oils (Cecutti and Agius 2008), and 30 days for synthetic oils (Haigh 1995). The bio vegetable oil that was used in this study also achieved a high degree of biodegradability - within 3 weeks (BIPOL L1 2017). The decomposition time of oils depends on many factors, including temperature, humidity, quantity and type of bacteria, quantity of oxygen, and other biological, ecological and physical factors (Stanovský *et al.* 2013). Additionally, temperature can have a strong impact on biodegradation efficiency (Ribicic *et al.* 2018; Skoupý *et al.* 2010). Ribicic *et al.* (2018) found

that different oil types may influence degradation rates and microbial community structure, especially at low temperatures.

The oil used for lubrication enters the forest environment directly and completely (Skoupý 2004). Bio-lubricants of vegetable origin do not migrate as deep as the mineral oils, but none of these compounds migrate further than 60 cm in depth in the soil within a certain period of time (Cecutti and Agius 2008). A chainsaw requires 0.05 litres of lubricating oil to produce 1m³ of wood, while a harvester needs less than half that amount of lubricating oil (i.e. only 0.02 litter) (Nowak *et al.* 2019). For example, in the state forest enterprise of Slovakia alone, 1.8 million litres of oil were spilt into the soil from chain saw operation alone (Stanovský *et al.* 2013). Oil pollution causes serious damage to soils, due to the physicochemical processes leading to a change in the distribution of organic matter. Consequently, the correct functioning of the ecosystem may be disturbed (Abosedo 2013).

Soil type and permeability have an impact on how oils affect the environment (Vähäoja *et al.* 2005). The properties of forest soils vary depending on the parent material, i.e. igneous or sedimentary rocks and Neogene-Quaternary sediments (Leitgeb *et al.* 2019). Forest soils are generally characterized by deeply rooted trees, wide varieties of soil-dwelling organisms, and recycling of organic matter and nutrients, including wood (Boyle 2005). The soils in forested areas are primarily affected by harmful and trace elements that result from atmospheric deposition (Baize and Oort 2014). These atmospheric pollutants have an effect on soil chemical properties, which modify solubility, mobility and availability of soil elements to plants (Tyler and Olsson 2002). The toxicity of heavy metals and their availability to forest habitats increase due to soil acidification caused by sulphur deposition (Temminghoff *et al.* 1997). Physical site manipulations in forest harvesting such as mechanical removal of competing vegetation and forest floor organic matter can alter soil physical properties such as porosity, infiltration capacity, and susceptibility to erosion. Crucial parameters that can positively influence the retention capacity of forest soils include the humus concentration, pH and saturation levels (Utermann *et al.* 2019).

Biodegradation of mineral and synthetic base oils is well documented and therefore we focused on the study of biodegradability impacts on vegetable oils, as they are commonly used in forestry. The aim of this study was to determine the effects of biodegradable lubricant oil on changes in the element composition of forest soils.

Material and Methods

Study area and sample collection

The site where sampling was performed is located in the National nature reserve (NNR) Slnčné skaly in Rajecká basin, Slovakia. The area of the NNR Slnčné Skaly is morphologically formed from dolomite. Field research took place from between 3 February and 24 March 2017. The altitude of the field was 550 meters above sea level. The sampling

site was approximately one hectare in size, and forested with non-native black pine (*Pinus nigra*) and common spruce (*Picea abies*). In the field harvesting occurred in a ratio of 70 % common spruce to 30 % black pine. Trees were sawed by standard technique (Slovak technical standard STN 48-00-50), using the principle of directional sawing with two cuts. After cutting the trees, a soil sampling methodology was developed. Ten stumps of spruce with a minimum distance of ten meters from one another were selected. The oil was preserved mainly on the soil surface under the point of cut. Soil samples were taken once per week around each stump. The soil samples had a base of limestone bedrock. We placed the obtained soil samples in 10 x 20 cm PVC bags. Samples were taken in a semi-circular shape around the stumps for eight weeks, totalling 80 samples from ten stumps. In order to establish the time distribution of the decomposition of biodegradable oil we used, control samples were necessary. These were obtained at a distance of ten meters from the upper edge of the stumps up the slope. A total of 80 control samples were collected over eight weeks. All together 160 soil samples were collected. To harvest trees we used standard forestry tools, including OLEO-MAC 947 handsaw and the HUSQVARNA 365 XP. These chainsaws are commonly used in forestry for different purposes. Both are powered by BA 95 fuel mixed 1 : 50 with STIHL HP self-mixing oil. Bipol biodegradable vegetable-based lubricating oil was used in both chainsaws.

Laboratory and statistical analyses

Soil samples were dried at 70° C for 12 h in a Memmert IF 160 laboratory Plus dryer (Mettmert, Germany). All samples were ground and homogenized into a fine dust in the Retsch Cryomill. The samples were analysed by X-ray fluorescence, using the hand-held XRF Spectrometer DELTA CLASSIC (Innov-X Systems, Inc., Woburn, MA, USA). We used multiple-beam measurement, in which every measurement consisted of 3 beams for 80 seconds, repeated three times, and then averaged. The results were given in ppm (part per million) units. The minimum value of a particular element represented the current detection limit of the spectrometer for the measured material. We used an additional calibration matrix to correctly measure for the specific needs of plant material analysis using certified plant standards INCT-PVTL-6 (ICHTI, Poland) and BCR-19, as well as NIST 1575a for the soils. The DELTA Spectrometer is designed for accurate investigation of heavy metals, transition metals, as well as rare earth elements. This instrument has a high analytical accuracy and precision of measurements (Innov-X Systems 2010). In cases of rare earth elements XRF measurements correspond with AAS results, but the spectrometer measures several light elements (mainly P) in wider limits. The XRF spectrometer can be used to determine variability and interrelationships of elements in samples by using multivariate statistical analyses. In our study, the effect of elements was evaluated by principal component analysis (PCA) which is widely used in ecotoxicological studies. It is a variable reduction technique that maximizes the amount of variance

accounted for in the observed variables by a smaller group of variables called components or factors.

We repeated measurements with certified standards, to demonstrate repeatability. The standard deviation (SD) was stable and minimal for all repeated measurements for measured elements. Control measurements of standard reference materials were consistent with the certified values within the uncertainty limit of <10 % (RSD) for relative standard deviation. The detection limits change for each sample and for each element during current measurements, therefore it is not possible to state the detection limits in the methodology. The minimum detection limit of the device is 1 ppm.

Results

According to the results of PCA, out of the 16 principal components only the first 4 components account for meaningful amounts of variance in the investigated plots (Table 1).

The highest variance of factor 1 reflects differences in soil composition among different plots (Table 2). Factor 1 (K, Ti, Cr, Mn, Fe, Rb, Sr, Zr, Ba) has a major effect on the soil and concentrations of these elements simultaneously increase or decrease. In plots 7 to 10, the elements that comprise factor 1 increase (Fig. 1a). Factor 1 shows different effects of lubricant oil on various types of soils. However, in Fig. 1a, there is a difference between oil and control plots, with significant higher concentrations of the investigated elements (K, Ti, Cr, Mn, Fe, Rb, Sr, Zr, Ba) found in control plots. The date of sample collection does not have a significant effect on the soil element composition (Table 3), although the elements were slightly depleted from the oil plots approximately three weeks into the experiment (Fig. 1b).

Factor 2 clearly shows that more calcium appeared in the control plots (Fig. 2a). The oil has an overall negative effect on calcium binding in the soil. The effect of oil on calcium concentration is not significant because the oil tends to act on the binding of calcium in the soil after approximately 5 weeks (Fig. 2b).

According to factor 3, there are clearly differences in the accumulation of S and Pb in soils from plots 7 – 10 (Fig. 3a). The concentrations of S and Pb tended to increase in oil plots (Fig. 3a), however this effect mainly occurred in the second half of the experiment (Fig. 3b).

In factor 4, the presence of oil presumably suppressed the amount of copper in the soil in plots 6 through 9. More copper remains in the control samples (Fig. 4a). However, the effect of lubricant oil on the binding of copper in the soil could not be established between different types or dates of samples and plots (Fig. 4a, b). There is evidently a large variance between individual plots.

Discussion

We found that oil may have a different effect on different types of soil or different plots. This phenomenon is mainly evident in factor 1 (Table 2). Amounts

of K, Ti, Mn, Cr, Fe, Rb, Sr, Zr and Ba significantly decreased in oil plots 7 to 10 (Fig. 1a). Decomposition of plant material highly influences the concentration of nutrients in forest soils (Aerts and Chapin 1999). The amount of litter and the thickness of organic soil horizon have significant impact on the concentration of nutrients, such as K (Pompeani *et al.* 2018). The decline in bioavailable K in the oil soil suggests its removal by mineralization (Qualls 2000) and subsequent utilization by plants. Mineralization increases the bioavailability of the nutrients in decomposing organic compounds for plants. The process of oil biodegradation can, in some cases, lead to complete mineralization of organic matter into carbon dioxide, water, inorganic compounds, and cell protein, or the breakdown of complex organic contaminants into other simpler organic compounds by microorganisms (Das and Chandran 2011). Decreasing soil nutrients, minerals and trace elements may be also caused by forest harvesting alone. This removes elements from the system in larger quantities at once (Federer *et al.* 1989). We found that time plays a significant role in the effect of biodegradable lubricant oil on soil element elimination. The depletion of elements from the soil starts approximately three weeks after the beginning of the experiment (Fig. 1b) and this time period corresponds to the estimated time of degradation of oil that was used in this study.

Soil Ca content has a fundamental effect on tree growth or indirect effects on soil pH. The content of Ca in soil is essential for multiple ecosystem processes, including soil organic matter decomposition and availability of nutrients such as N and P (Page and Mitchell 2008). Surface geology, soil depth, landscape position, hydrology, and slope characteristics are considered crucial internal landscape drivers of forest Ca cycling and export (McLaughlin 2014). We found that biodegradable oil has a negative effect on the binding of Ca in the soil. Thus, forest harvesting practices that utilize lubricant oil (biodegradable or unbiodegradable) may have an impact on forest Ca cycling (Zetterberg *et al.* 2013). A soil's capacity to neutralize acids is required for forest growth, as it establishes conditions for soil food-web functions and nutrient cycling (Park *et al.* 2008). However, forestry practices such as harvesting and regeneration may further intensify soil acid cation and anion production and leaching of calcium from the soil (Likens *et al.* 1998). The impact of lubricant oils can be intensified by clear-cutting of forests, which leads to radical changes in the underlying soil, humus layer, and soil chemistry (Berthelsen and Steinnes, 1995). Long-term acidification of forest soils can lead to changes in the Ca dynamic, which may subsequently affect nutrient limitation (Leys *et al.* 2016). Calcium is an important element for neutralizing soil acidity in forests (Dijkstra 2003). The effects of lubricant oil differed between plots, however, increased Ca depletion in plots 7 - 10 may be a result of variations in Ca cycling between various tree species, which affects nutrient balances in the soil (Dijkstra 2003). The common spruce was predominant on the plots that were investigated throughout this study, but black pine was also observed within the sample area.

We found that soils reflect a high variance in element compositions. Surface soil systems are unstable with respect to heavy metal accumulation and large concentration variations are frequently

Element	Factor 1	Factor 2	Factor 3	Factor 4
S	-0.16	-0.10	0.74	0.24
Cl	-0.61	0.10	-0.22	-0.02
K	0.94	-0.02	-0.00	-0.10
Ca	0.35	-0.81	0.25	-0.18
Ti	0.98	0.06	-0.03	-0.05
Cr	0.82	0.39	-0.11	0.04
Mn	0.97	-0.08	0.03	-0.04
Fe	0.93	0.29	0.10	0.08
Cu	-0.10	0.34	0.43	-0.82
Zn	-0.68	0.40	0.24	-0.01
Rb	0.95	0.23	-0.06	0.07
Sr	0.81	-0.22	0.10	-0.04
Zr	0.97	0.11	-0.11	-0.02
Mo	-0.70	0.54	-0.06	0.02
Ba	0.95	0.24	-0.03	-0.02
Pb	0.28	0.25	0.64	0.34
Variance (%)	57.8	10.7	8.5	5.6

Table 1. Component weights of the principal component analysis at the first four most important factors. Factors indicate the process of element manifestation in the examined soils.

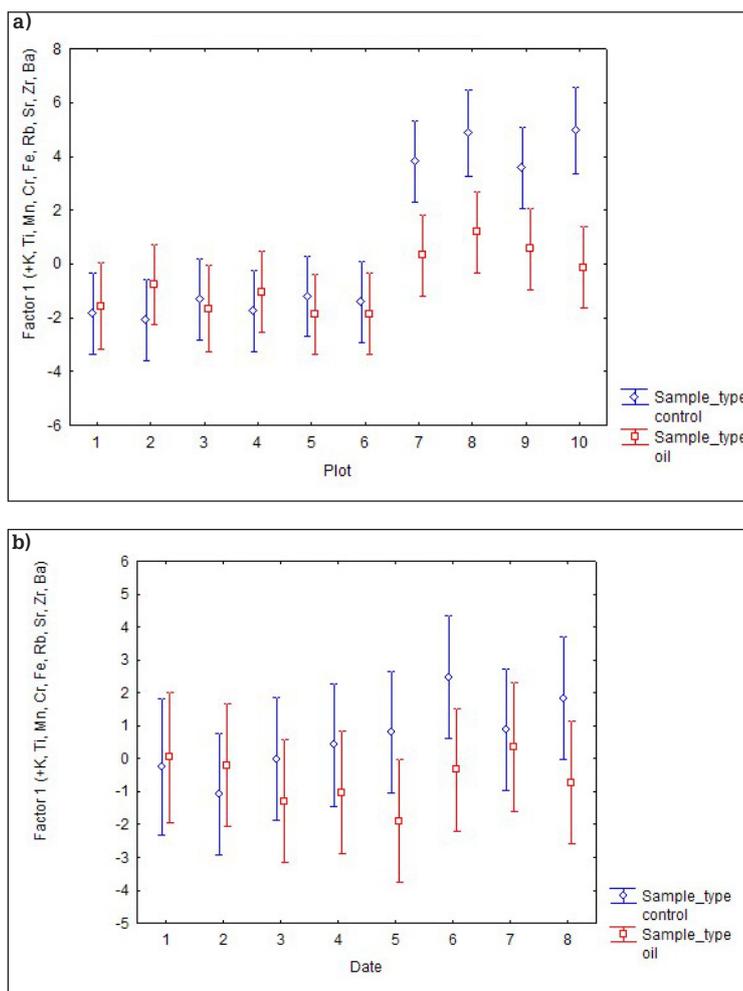


Fig. 1. Oil significantly influenced concentrations of many elements in the soil. Amounts of K, Ti, Mn, Cr, Fe, Rb, Sr, Zr and Ba significantly decreased at the oil plots from 7 to 10 against to control plots (a), and the elements were reduced from the soil approximately three weeks after beginning of the experiment (b). Two-way ANOVA of principal component scores is presented in Tables 2 and 3.

Factor	Plot	Sample type	Plot/ Sample type interaction
Factor 1	F (9, 136) =13.97, p =0.000***	F (9, 136) =17.55, p =0.000***	F (9, 136) =4.08, p =0.000***
Factor 2	F (9, 136) =5.85, p =0.000***	F (9, 136) =4.04, p =0.046*	F (9,136) =0.94, p =0.494
Factor 3	F (9, 136) =0.54, p =0.846	F (9, 136) =5.06, p =0.026*	F (9, 136) =1.11, p =0.362
Factor 4	F (9, 136) =0.70, p =0.078	F (9, 136) =0.12, p =0.727	F (9, 136) =1.21, p =0.295

Table 2. Differences in the effects of element concentrations in soil samples between plots and sample type. Two way ANOVA of principal component scores. *** p < 0.001; ** p < 0.01; * p < 0.05.

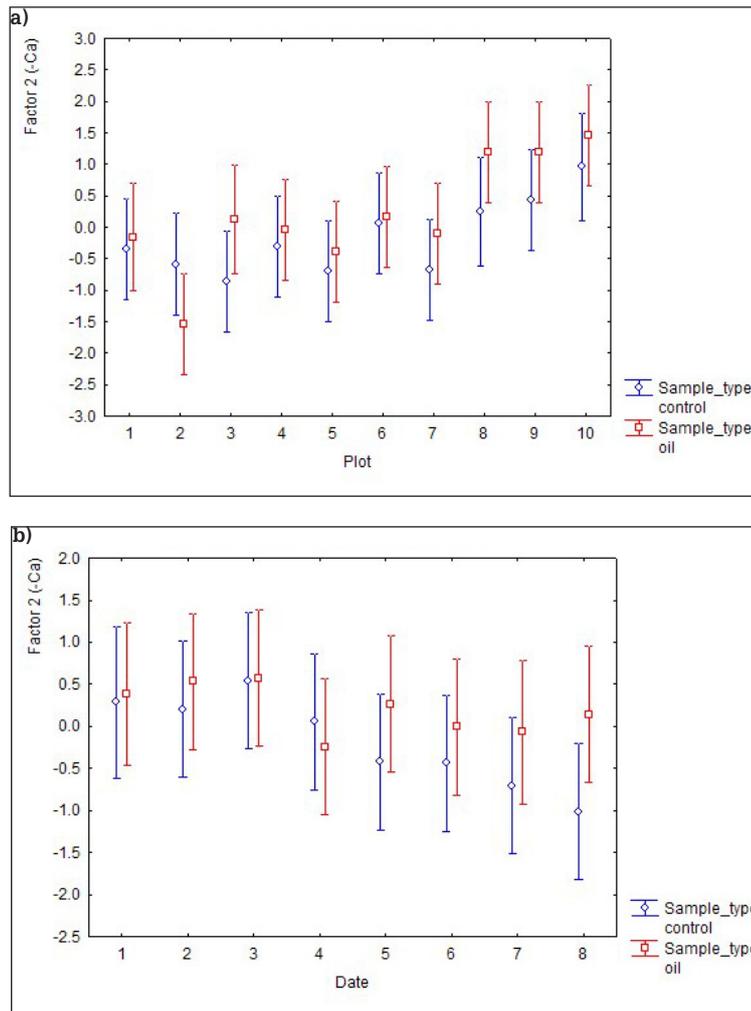


Fig. 2. Oil significantly removes calcium at plot 7 to 10 (a). Although the calcium tended to decrease after five weeks from the beginning of the experiment, the difference in this phenomenon was not significant between oily and control samples (b). Two-way ANOVA of principal component scores is presented in Tables 2 and 3.

found within small areas (Berthelsen and Steinnes 1995). Heavy metals have an affinity for accumulation in surface organic layers and consequently affect the biological activity in forest soils (Hernandez *et al.* 2003). Stefanowicz *et al.* (2009) found that the functional diversity of bacterial communities in soil decreased with increasing metal concentrations in forest ecosystems. We found that the oil samples had higher levels of lead and sulphur than the control

samples. Sulphur significantly decreases soil pH and increases the availability and mobility of heavy metals (Cui *et al.* 2004). One of the most important soil parameters affecting metal content in bioavailable forms is pH (Takáč *et al.* 2009). Low pH and a high level of organic matter in soil result in high mobility of heavy metals (Muhammad *et al.* 2011). An increase in Pb content in the soils is due to both the influence of humus dynamics and the close correlation

Factor	Date	Sample type	Date / Sample_type interaction
Factor 1	F (7, 140) =0.98, p =0.445	F (7, 140) =7.06, p =0.009***	F (7, 140) =1.07, p =0.383
Factor 2	F (7, 140) =1.59, p =0.142	F (7, 140) =3.39, p =0.068	F (7, 140) =0.60, p =0.754
Factor 3	F (7, 140) =7.30, p =0.000***	F (7, 140) =7.05, p =0.009***	F (7, 140) =2.41, p =0.023**
Factor 4	F (7, 140) =1.71, p =0.112	F (7, 140) =0.13, p =0.714	F (7, 140) =0.90, p =0.508

Table 3. Differences in the effects of element concentrations in soil samples between dates and sample type. Two way ANOVA of principal component scores. *** p < 0.001; ** p < 0.01; * p < 0.05.

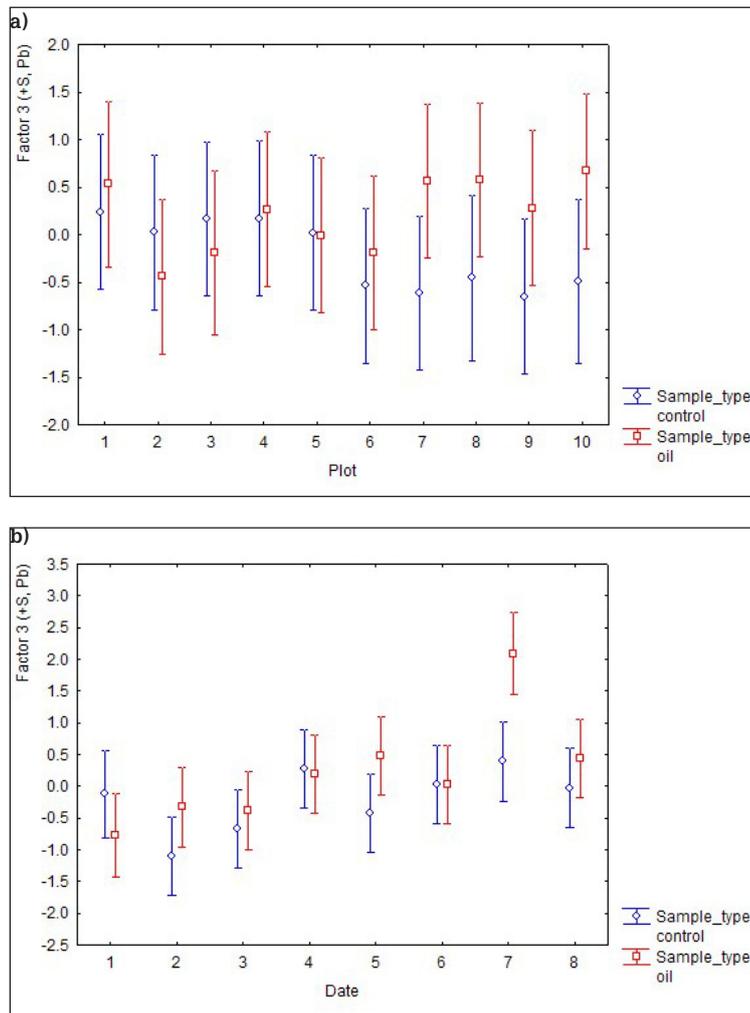


Fig. 3. Acidification by sulphur and synergic pollution by lead are more depended on the plot than on the sample type (**a**); Table 1) and mainly occurred in the second half of the experiment (**b**); Table 3.).

between measurements of heavy metals and organic matter (Utermann *et al.* 2019). The behaviour of Pb in organic surface soils is determined by soil chemical factors (Berthelsen and Steinnes, 1995). Generally, Pb availability increases as soil pH decreases (Siebielec *et al.* 2006). Soil contaminated by sulphur is characterized by an increased bioavailability of Pb in roots and plants in the forest. We found that sulphur and lead in forest soils are closely related. Similar findings were

reported by Holah *et al.* (2010), demonstrating that increasing concentrations of sulphur caused a considerable increase in lead content in plants.

We found that biodegradable lubricant oils have an insignificant negative impact on the amount of copper in the soil (Fig. 4a, 4b). In most cases, more copper was present in control samples. Cu is strongly associated with biomass in organic surface soils (Berthelsen and Steinnes 1995).

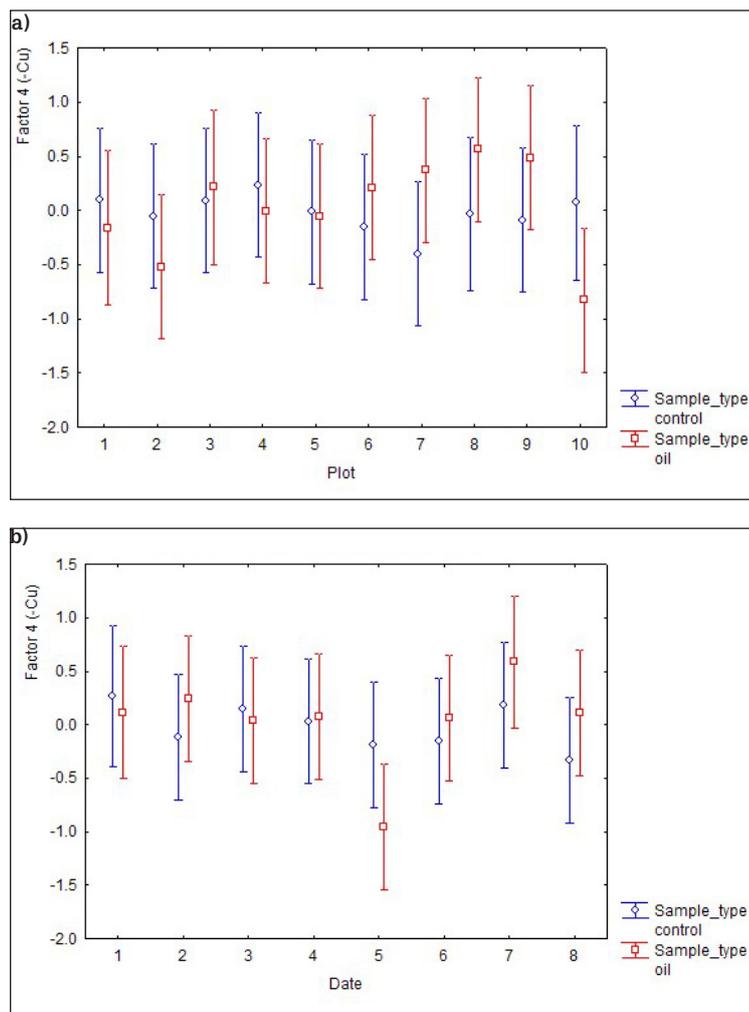


Fig. 4. Amount of copper did not significantly differ in dependence on type of samples, plots (a) or experiment chronology (b) (Tables 2 and 3).

According to Tyler and Olsson (2002), most of the Cu occurs as a soluble complex in organic matter. This finding may be related to the increase in organic litter present in plots with standing trees, consistent with those that used for the collection of control samples.

We can conclude, therefore, that biodegradable lubricant oils can influence the composition and concentration of elements in soils, regardless of this product's rapid degradation and very low eco-toxicity (Stanovský *et al.* 2013). There is an assumption that the biodegradation of bio-oils affects mineralization processes, pH, nutrient availability, and the mobility and bioavailability of heavy metals such as Pb. This study is the first step in analysing the effect of vegetable oils on soil processes, but these issues deserve further exploration, as there is no doubt that biodegradable lubricant oils are significantly less harmful than synthetic or mineral oils.

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References

- Abosedo, E.E. 2013: Effect of crude oil pollution on some soil physical properties. *J. Agric. Vet. Sci.*, **6**: 14-17.
- Aerts, R. and Chapin III, F.S. 1999: The mineral nutrition of wild plants revisited: A re-valuation of processes and patterns. *Adv. Ecol. Res.*, **30**: 1-67.
- Bartz, J.W. 1998: Lubricants and the environment. *Tribol. Int.*, **31**: 35-47.
- BIPOL_L1. 2017: Chain lubricating oil. RIWALL. Product specification. Online: https://www.mountfield.sk/olejna-mazanie-retazi-bipol-1-1-1-phm1008?gclid=EAlaIQo bChMlzqfBoMyG7QIVk_hrCh2Z8ARAEAAAYASAAEg-K6cvD_BwE. (retrieved 25.4.2020).
- Baize D., van Oort F. 2014: Potentially Harmful Elements in Forest Soils. In: *PHEs, Environment and Human Health* (eds. C. Bini and J. Bech), pp. 1.51-198 Springer, Dordrecht.
- Berthelsen, B.O. and Steinnes, E. 1995: Accumulation patterns of heavy metals in soil profiles as affected by forest clear-cutting. *Geoderma*, **66**: 1-14.
- Boyle, J.R. 2005: Forest soils. In: *Encyclopedia of Soils in the Environment* (ed. D. Hillel), pp. 73-79. Academic Press, Oxford, UK, St Louis, MO.
- Cecutti, Ch. and Agius, D. 2008: Ecotoxicity and biodegradability in soil and aqueous media of lubricants used in forestry applications. *Bioresour. Technol.*, **99**: 8492-8496.
- Cui, Y., Dong, Y., Li, H. and Wang, Q. 2004: Effect of elemental sulfur on solubility of soil heavy metals and their uptake by maize. *Environ. Int.*, **30**: 323-328.

- Das, N. and Chandran, P. 2011: Microbial degradation of petroleum hydrocarbon contaminants: an overview. *Biotechnol. Res. Int.*, **11**: 1-13.
- Dijkstra, F.A. 2003: Calcium mineralization in the forest floor and surface soil beneath different tree species in the northeastern US. *For. Ecol. Manag.*, **175**: 185-194.
- Erhan, S.Z. and Asadauskas, S. 2000: Lubricant basestocks from vegetable oils. *Ind. Crops. Prod.*, **11**: 277-282.
- Federer, C.A., Hornbeck, J.W., Tritton, L.M., Martin, C.W., Pierce, R.S. and Smith, C.T. 1989: Long-term depletion of calcium and other nutrients in eastern US forests. *Environ. Manage.*, **13**: 593-601.
- Haigh, S.D. 1995: Fate and effects of synthetic lubricants in soil: biodegradation and effect on crops in field studies. *Sci. Total Environ.*, **168**: 71-83.
- Hernandez, L., Probst, A., Probst, J.L. and Ulrich, E. 2003: Heavy metal distribution in some French forest soils: evidence for atmospheric contamination. *Sci. Total Environ.*, **312**: 195-219.
- Holah, S., Kamel, M.M., Taalab, A.S., Siam, H.S., El-Rahman and Eman, A. 2010: Effect of elemental sulfur and peanut compost on the uptake of Ni and Pb in basil and peppermint plants grown in polluted soil. *Int. J. Acad. Res.*, **2**: 211-219.
- Innov-X Systems. 2010: User Manual. Delta™ Family: Handheld XRF Analyzers.
- Lauhanen, R., Kolppanen, R., Takalo, S., Kuokkanen, T., Kola, H. and Valimäki, I. 2000: Effects of biodegradable oils on forest machines and forest environment. In: *Proceedings of the Scientific Conference on Forest and Wood Technology vs. Environment*, pp. 203-207. Brno.
- Leitgeb, E., Ghosh, S., Dobbs, M., Englisch, M. and Michel, K. 2019: Distribution of nutrients and trace elements in forest soils of Singapore. *Chemosphere*, **222**: 62-70.
- Leys, B.A., Likens, G.E., Johnson, C.E., Craine, J.M., Lacroix, B., and McLaughlan, K.K. 2016: Natural and anthropogenic drivers of calcium depletion in a northern forest during the last millennium. *PNAS*, **113**: 6934-6938.
- Likens, G.E., Driscoll, C.T., Buso, D.C., Siccama, T.G., Johnson, C.E., Lovett, G.M., Fahey, T.J., Reiners, W.A., Ryan, D.F., Martin, C.W. and Bailey, S.W. 1998: The biogeochemistry of calcium at Hubbard Brook. *Biogeochemistry*, **41**: 89-173.
- McLaughlin, J.W. 2014: Forest soil calcium dynamics and water quality: implications for forest management planning. *Soil. Sci. Soc. Am. J.*, **78**: 1003-1020.
- Muhammad, S., Shah, M.T. and Khan, S. 2011: Heavy metal concentrations in soil and wild plants growing around Pb-Zn sulfide terrain in the Kohistan region, northern Pakistan. *Microchem. J.*, **99**: 67-75.
- Nowak, P., Kucharska, K. and Kaminski, M. 2019: Ecological and health effects of lubricant oils emitted into the environment. *Int. J. Environ. Res. Public Health*, **16**: 3002.
- Page, B.D. and Mitchell, M.J. 2008: Influences of a calcium gradient on soil inorganic nitrogen in the Adirondack Mountain, New York. *Ecol. Appl.* **18**: 1604-1614.
- Park, B.B., Yanai, R.D., Fahey, T.J., Bailey, S.W., Siccama, T.G., Shanley, J.B., and Cleavitt, N.L. 2008: Fine root dynamics and forest production across a calcium gradient in northern hardwood and conifer ecosystems. *Ecosystems*, **11**: 325-341.
- Pompeani, D.P., McLaughlan, K.K., Chileen, B.V., Wolf, K.D., and Higuera, P.E. 2018: Variation of key elements in soils and plant tissues in subalpine forests of the northern Rocky Mountains, USA. *Biogeosci. Discuss.*, 1-19.
- Ribicic, D., McFarlin, K.M., Netzer, R., Brakstad, O.G., Winkler, A., Holst, M.H. and Størseth, T.R. 2018: Oil type and temperature dependent biodegradation dynamics - Combining chemical and microbial community data through multivariate analysis. *BMC Microbiol.*, **18**: 1-15.
- Qualls, R.G. 2000: Comparison of the behavior of soluble organic and inorganic nutrients in forest soils. *For. Ecol. Manag.*, **138**: 29-50.
- Siebielec, G., Stuczyński, T. and Korzeniowska-Puculek, R. 2006: Metal bioavailability in long-term contaminated Tarnowskie Gory soils. *Pol. J. Environ. Stud.*, **15**: 121-129.
- Skoupý, A. 2004: Biologically degradable oils at working with power saws. *J. For. Sci.*, **50**: 542-547.
- Skoupý, A., Klvac, R. and Hosseini, S. 2010: Changes in the external speed characteristics of chainsaw engines with the use of mineral and vegetable oils. *Croat. J. For. Eng.*, **31**: 149-155.
- Stanovský, M., Schürger, J., Jankovský, M., Messingerová, V., Hnilica, R. and Kučera, M. 2013: The Effect of lubricating oil on temperature of chainsaw cutting system. *Croat. J. For. Eng.*, **34**: 83-90.
- Stefanowicz, A.M., Niklińska, M. and Laskowski, R. 2009: Pollution-induced tolerance of soil bacterial communities in meadow and forest ecosystems polluted with heavy metals. *Eur. J. Soil Biol.*, **45**: 363-369.
- Takáč, P., Szabová, T., Kozáková, L. and Benková, M. 2009: Heavy metals and their bioavailability from soils in the long-term polluted Central Spiš region of SR. *Plant Soil Environ.*, **55**: 167-172.
- Temminghoff, E.J., Van der Zee S.E. and de Haan F.A. 1997: Copper mobility in a copper contaminated sandy soil as affected by pH and solid and dissolved organic matter. *Environ. Sci. Technol.*, **31**: 1109-1115.
- Tyler, G. and Olsson, T. 2002: Conditions related to solubility of rare and minor elements in forest soils. *J. Plant. Nutr. Soil Sci.*, **165**: 594-601.
- Vähöja, P., Roppola, K., Välimäki, I. and Kuokkanen, T. 2005: Studies of biodegradability of certain oils in forest soil as determined by the respirometric BOD OxiTop method. *Int. J. Environ. Anal. Chem.*, **85**: 1065-1073.
- Utermann, J., Aydın, C.T., Bischoff, N., Böttcher, J., Eickenscheidt, N., Gehrmann, J., König, N., Scheler, B., Stange, F. and Wellbrock, N. 2019: Heavy metal stocks and concentrations in forest soils. In: *Status and Dynamics of Forests in Germany* (eds. N. Wellbrock and A. Bölte), pp. 199-229. Springer, Cham, Switzerland.
- Zetterberg, T., Olsson, F.A., Löfgren, S., von Brömssen, C., and Brantberg, P.O. 2013: The effect of harvest intensity on long-term calcium dynamics in soil and soil solution at three coniferous sites in Sweden. *For. Ecol. Manag.*, **302**: 280-294.