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Biodegradation of rubber particles in soil

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Abstract

The biodegradation of rubber particles in rubber-soil mixtures at different rubber contents was monitored by the carbon dioxide production. The cumulative carbon dioxide production was modelled according to a two parameter exponential function. The model provides an excellent fit ($R^2 > 0.98$) for the observed data. The two parameters yield a reliable estimate of the half-life for the process observed, but estimation of the true half-life of rubber in soil will need more research.

Introduction

Rubber particles obtained from discarded material have many possible applications. Some examples are athletic tracks, drainage pipes, kindergarten playgrounds and recreation areas, shoe soles and soil conditioner (Recycling Council of Ontario, 1992). When rubber particles are used in contact with soil, it is useful to know how long they will last.

The degradation rate of rubber particles will depend on their size. The question how fast the degradation will occur has not yet received extensive attention. The composition of rubber as presented in Table 1 suggests that the biodegradation will occur in stages. Not much research has been conducted to estimate the longevity of rubber particles in soil.

This article presents the results of an incubation experiment with different mixtures (by weight) of rubber particles and soil. It also presents an estimate of the longevity of rubber particles in soil under the applied conditions.

Materials and methods

The incubation study was carried out with 1 litre standard mason jars. The exact volume of the jars was 990 ml. Soil was taken from the Guelph Turfgrass Institute, and was dried and sieved trough a 2mm sieve. The soil was classified as Guelph loam, with 49.2% sand, 39.2% silt and 11.6% clay. The organic matter content was 3.1%. The rubber particles had a mean diameter of 2.5 mm. The carbon content of rubber is 81.5% (Roy et al., 1990). CO_2 analysis was conducted on the departmental GOW MAC gas chromatograph. The GC was fit with a poropak Q Molecular Sieve 5A column. Helium was used as carrier gas and the GC was operated at 60 °C.

In the experiment 4 different treatments were used i.e. 10% rubber, 20% rubber, 30% rubber and 40% rubber. All as percentage of total weight, i.e. 22.2, 50, 85.7 and 133.3 g of rubber, respectively. Each jar contained the same amount of soil, i.e. 200 g. Because adding rubber to the soil meant adding a carbon source, $Ca(NO_3)_2$ was added to each treatment in order to keep the C:N-ratio at 10:1. Each treatment had its own control which received the same amount of $Ca(NO_3)_2$ for comparison. Soil and rubber were weighed into the jars and mixed. The water content was regulated at –100 kPa. This was done by determining the water content of the different treatments on a pressure plate apparatus. After mixing the soil and the rubber $Ca(NO_3)_2$ solution and water were added in calculated amounts. Also a small amount of $CaHPO_4$ solution was added to make sure there was a sufficient P supply. The experiment was designed to last 12 weeks. Three replicates of each

Table 1. Average rubber tire composition.

Constituent	Percentage by weight
Styrene-butadiene rubber	26.0 - 35.0
cis-Polybutadiene rubber	8.5 - 9.6
Natural rubber or isoprene	0 - 6.3
Butyle or Chorobutyle	0 - 3.3
Aromatic oil	0 - 20.0
Carbon black	24.7 - 27.8
Zinc oxide	1.0 - 2.8
Sulphur	1.0 - 1.4
Stearic acid	1.0 - 1–8
Additives (i.e. accelerators, antidegradants)	0 - 37.6
Fibres (including wire)	0 - 13.3

Source: Farcasiu 1993;Morison & Bourdays 1990; ASTM 1988; Winspeer 1968

treatment and its control, i.e. 24 jars were used. Each jar was fitted with a septum to enable sampling of the gas in the head space. All jars were kept in a constant temperature room at 20 °C. During these 12 weeks, CO_2 production was measured twice per week. After each CO_2 measurement the jars were opened to let the built up CO_2 escape and let fresh air in. This in order to have sufficient oxygen supply for growth.

The head space volume of the jars was measured by determining the volume of water occupying the same bulk space in a separate jar as the soil or soil/rubber mixture. Samples of 0.5 ml. of gas were taken from the head space volume via a gas syringe for CO_2 analysis and analysed on the GC. The concentration of CO_2 was expressed in ml per jar.

In order to see how much of the substrate was fixed into biomass, biomass C(arbon) analyses were conducted. The analyses were conducted according to the method of Voroney et al. (1993). This uses fumigation of a soil sample to make biomass C available for measurement. Biomass C is measured as the difference in 0.5 M K_2SO_4 extractable C between the fumigated and an unfumigated sample. The analyses were done on a Technicon Auto Analyzer colourimeter.

The amount of biomass produced from the rubber can then be calculated by subtracting the biomass of the control sample from the biomass of the rubber treated sample.

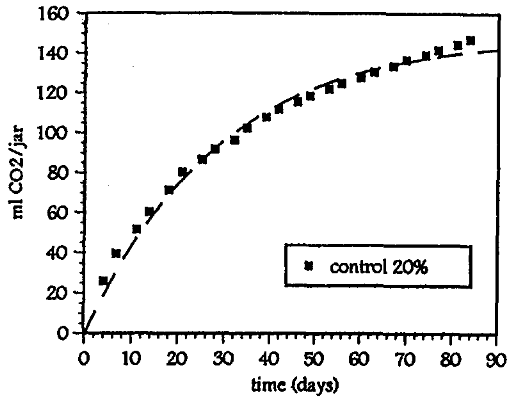

Figure 1. data with curve fit for the control 20%

Results and discussion

The results of the CO_2 measurements were plotted as cumulative production in ml per jar over time in days. The cumulative production was modelled according to:

$$Y = Y_{max} {}^{*}[1 - e^{(-\alpha * t)}]$$

where Y is the cumulative CO_2 concentration in ml per jar, Y_{max} the maximum CO_2 production also in ml per jar, t is the time in days and α is a degradation parameter with

$$\alpha = \frac{1n2}{T_{1/2}}(day^{-1}), \text{where} T_{1/2} \text{ is the}$$

half-life in days of the degrading material. For the controls the degrading material is soil organic matter. For the mixtures of soil and rubber the degrading material is the soil organic matter and the rubber.

First we will discuss the controls. The only variable here is the amount of $Ca(NO_3)_2$ added. Higher $Ca(NO_3)_2$ applications had a negative effect on CO_2 production at the beginning, but this effect disappeared during the experiment. All the fitted curves had an R^2 value higher than 98%. α decreased slightly with increasing nitrate application and Y_{max} increased slightly. We will present only the graph for the control of the 20% rubber treatment (Figure 1).

The equation for the curve presented in Figure 1 is:

$$Y = 1.49 * 10^2 * [1 - e^{(-3.49 * 10^{-2} * t)}],$$

obtained by regression (R^2 = 99.13%).

For all the controls $Y = Y_{max}$ represents 3.8% of the total organic carbon. The good fit of the exponential

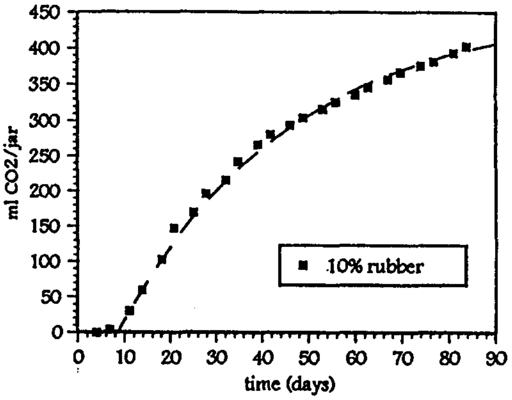

Figure 2. data and curve fit for the 10% rubber treatment.

curve justifies the use of first order kinetics to describe the degradation of the soils organic matter.

The data of the controls were each subtracted from their rubber treatment to ensure that the CO_2 production coming only from the rubber is used for the analysis. Each treatment showed a time lag of 200 hours (8.33 days) for CO_2 production to become significantly higher than its control. Therefore the model had to be changed to take this time lag into account. The new equation is:

$$Y = Y_{max} {}^*[1 - e^{(-\alpha*(t-8.33))}]$$

$$\text{with } \alpha = \frac{\text{In}2}{(T_{1/2} - 8.33)} .$$

With this equation the data were fitted. The result of using this equation was that the value of Y_{max} was not increasing linearly with the amount of rubber added. Statistical analyses proved that this discrepancy was the result of fitting with two variables. The Y_{max} values found with this equation were fitted by weighted linear regression. The equation found was $Y_{max} = 20.74{}^*R$ (R^2=99.93%) with R being the amount of rubber added to the jar in grams. With this equation new Y_{max} values were calculated and used as a constant for the next fit, now with only α as variable, of the exponential equation.

The data with their fitted curves are plotted in Figures 2,3,4 and 5. The R^2 values for all the fitted curves were above 99%. The fitted curves extended over time are put together in Figure 6.

The equations for the curves are:

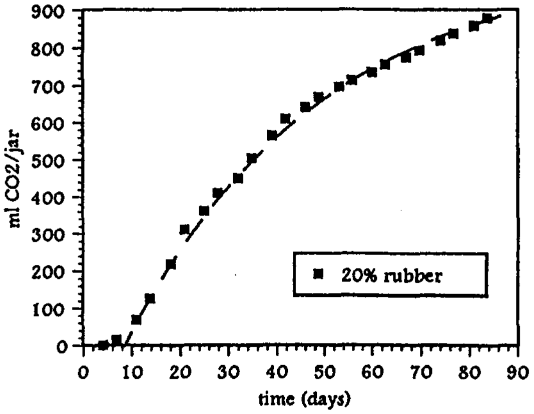

Figure 3. data and curve fit for the 20% rubber treatment.

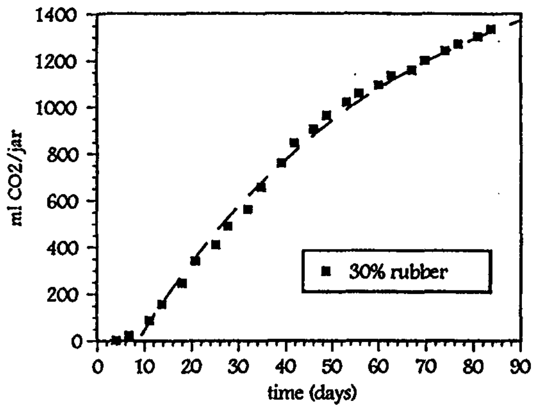

Figure 4. data and curve fit for the 30% rubber treatment.

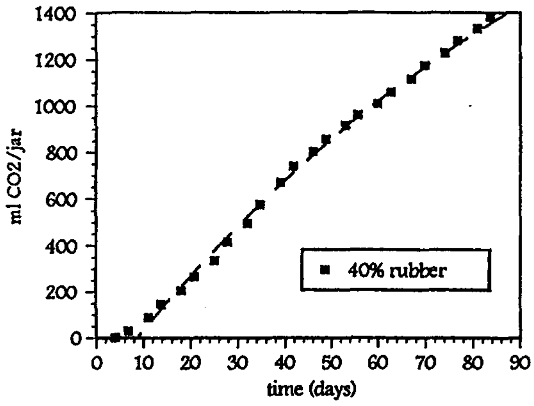

Figure 5. data and curve fit for the 40% rubber treatment.

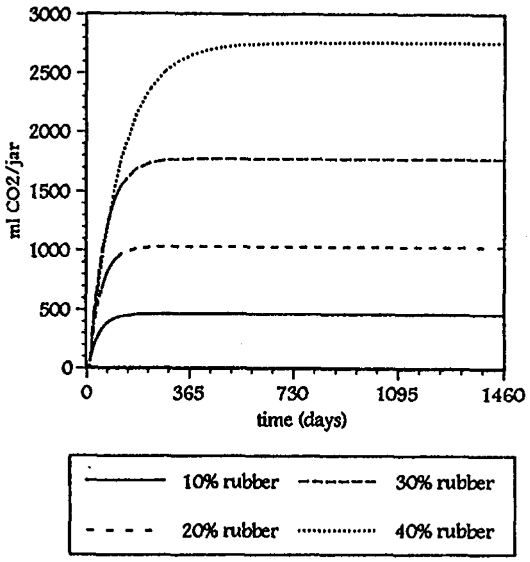

Figure 6. fitted curves as function of time.

10% rubber :

$$Y = 460^*[1 - e^{(-2.67*10^{-2}*(t-8.33))}]$$

$$R^2 = 99.24\%$$

20% rubber :

$$Y = 1037^*[1 - e^{(-2.47*10^{-2}*(t-8.33))}]$$

$$R^2 = 99.31\%$$

30% rubber :

$$Y = 1777^*[1 - e^{(-1.83*10^{-2}*(t-8.33))}]$$

$$R^2 = 99.06\%$$

40% rubber :

$$Y = 2764^*[1 - e^{(-8.98*10^{-3}*(t-8.33))}]$$

$$R^2 = 99.47\%$$

The value of Y_{max} now increases linearly with increasing rubber percentage. The value of α decreases with increasing rubber content indicating an effect of the degree of contact between the rubber and the soil on this degradation parameter.

The analysis for biomass C showed that the ratio CO_2-biomass was 80 × 20 for the rubber treatments. From this ratio the total amount of carbon degraded at $Y=Y_{max}$ could be calculated and from that the percentage of rubber degraded. The percentage of the total carbon applied that would be degraded at $Y=Y_{max}$ was calculated to be around 1.8%. The high value of R^2 shows that the degradation of rubber can be described by first order kinetics. Williams (1986) suggested that micro-organisms preferentially attack the stearic acid content of vulcanised rubber. Table I indicates that the average stearic acid content of vulcanised rubber is 1.0–1.8%. Based on the results that indicate that at Y_{max} around 1.8% of the total carbon present would be degraded, one can assume that stearic acid is being degraded. However this can not be verified with the results from this research.

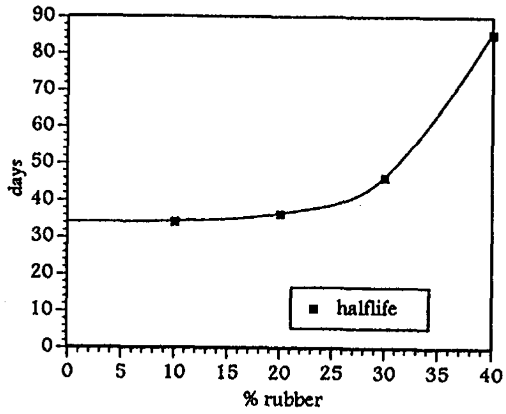

Figure 7. plot of half-lives with extrapolated curve.

Table 2. Half-life of the degrading component.

Treatment	half-life (days)
10% rubber	34.3
20% rubber	36.3
30% rubber	46.2
40% rubber	85.5

From the equations obtained by curve fitting the half-life of the degrading component was calculated.

Plotting the half-lives presented in table II and extrapolation to 0% rubber content gives an estimated half-life of 34 days (Figure 7).

At low rubber content the contact between rubber particles and soil is optimal giving the highest possible value for α, and the lowest value of $T_{1/2}$.

One cannot make an estimation of the longevity of rubber particles in soil based on the results shown. Probably only one step, the degradation of the most degradable component (presumably stearic acid), in the degrading process was observed. Following steps, for example the degradation of butadiene polymers, will have lower degradation rates than shown here, and therefore will be slower than the observed step.

However an indication of the minimum longevity of rubber particles in soil is interesting because of its practical value. Such a minimum longevity might be estimated assuming that the observed process will be repeated with the same degradation rate in the following steps of the degradation process.

For the 10% rubber mixture the time to reach 99% of Y_{max} for the first step, involving 1.8% of the total rubber, is 176 days. Degradation of all rubber in this mixture therefore would certainly require more, and probably much more, than 27 years.

Conclusions

The degradation of rubber particles in soil could be described by first order kinetics. The parameter α is probably depending on the degree of contact between soil and rubber.

Definite predictions for the longevity of rubber particles in soil are difficult, and cannot be made from the results shown here because only part of the degradation process was observed during the experiment.

Following processes will probably be much slower because micro-organisms tend to attack components which can be degraded more easily first.

Further research therefore has to be conducted to obtain better understanding of the processes involved. Understanding of these processes will help to obtain an estimate for the longevity of rubber particles in soil, especially where higher applications of rubber are concerned.

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