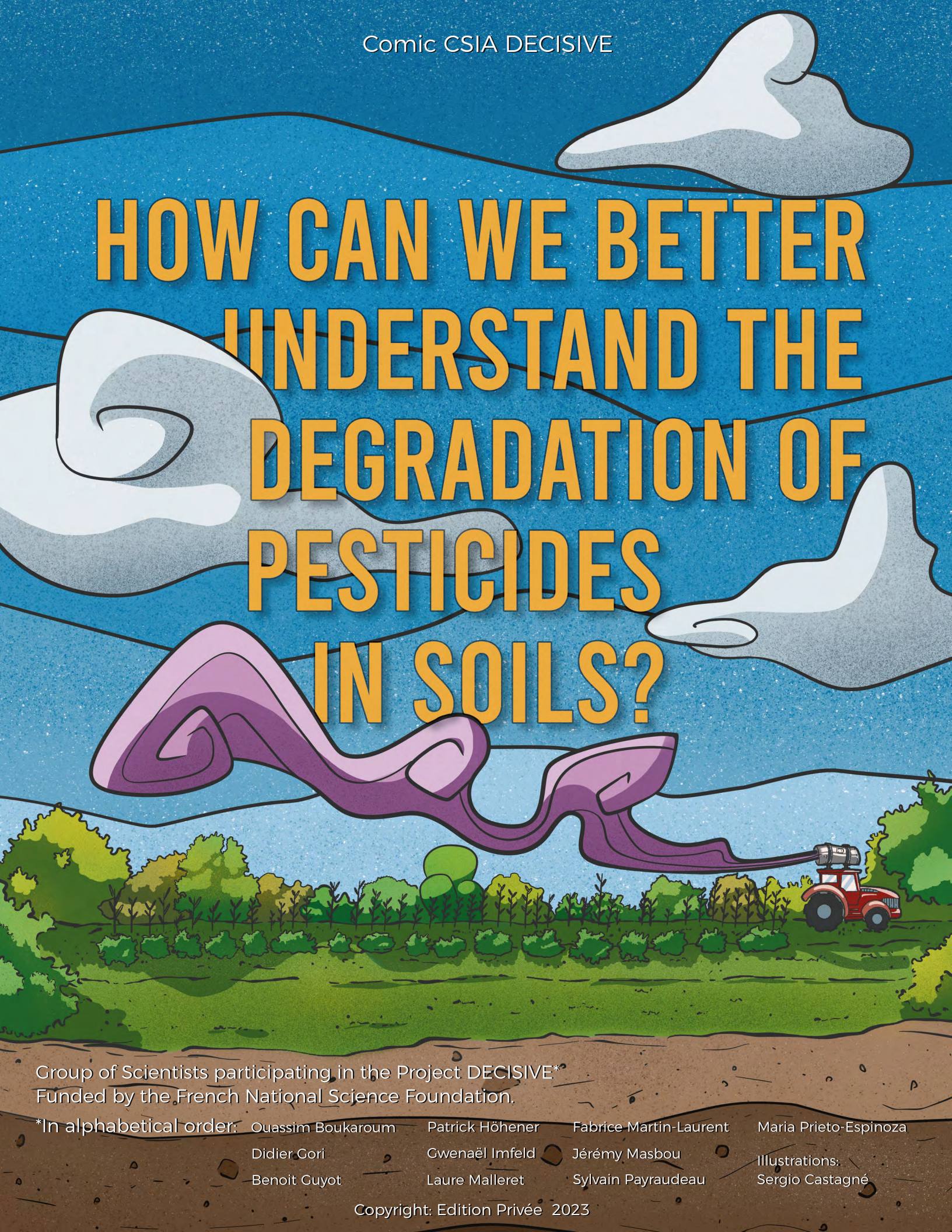


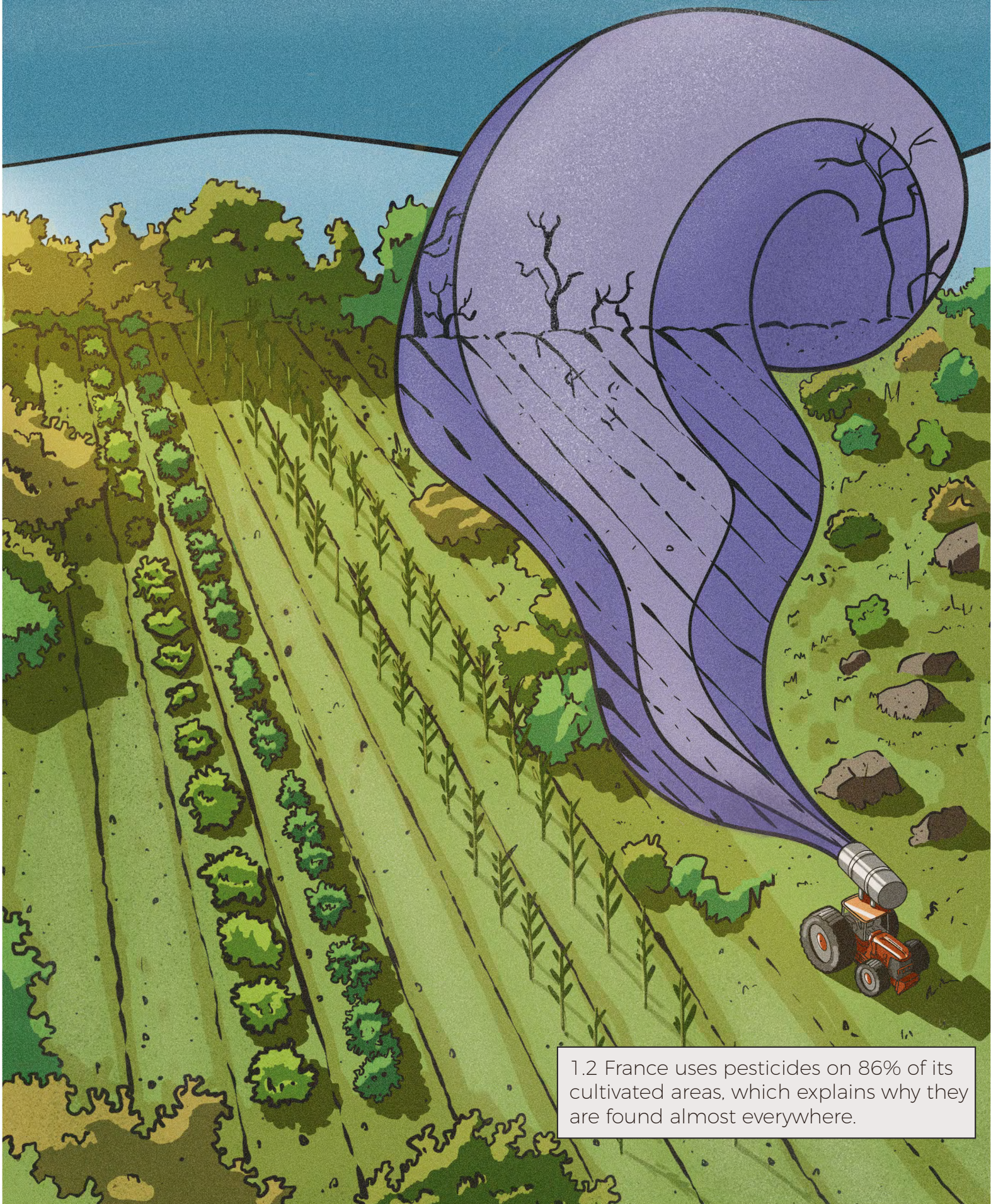
HOW CAN WE BETTER UNDERSTAND THE DEGRADATION OF PESTICIDES IN SOILS?



Group of Scientists participating in the Project DECISIVE*
Funded by the French National Science Foundation.

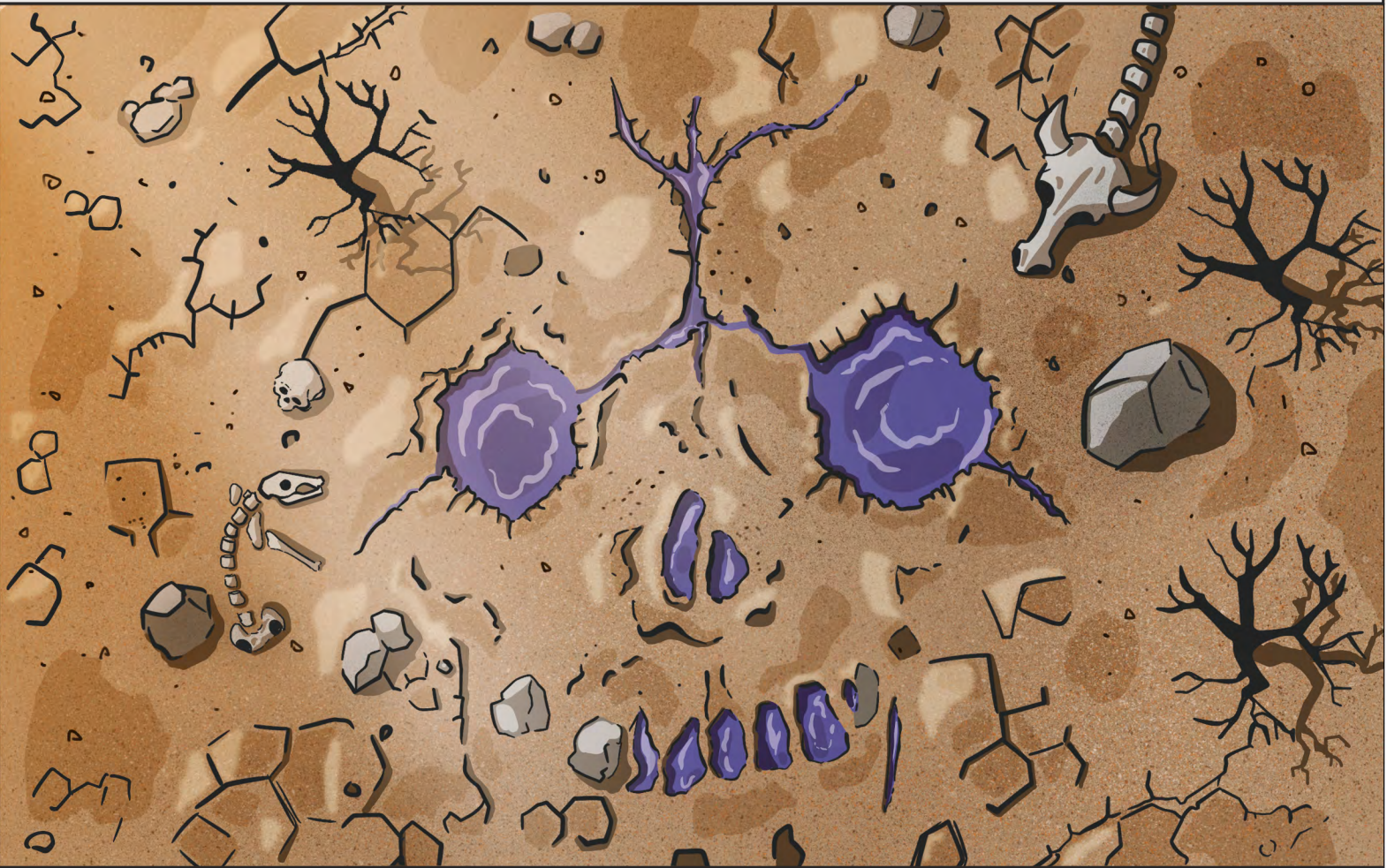
*In alphabetical order: Ouassim Boukaroum Patrick Höhener Fabrice Martin-Laurent Maria Prieto-Espinoza
Didier Gori Gwenaël Imfeld Jérémy Masbou Illustrations:
Benoit Cuyot Laure Malleret Sylvain Payraudeau Sergio Castagné

1.1 Pesticides are used in an agricultural model called conventional agriculture to suppress weeds (herbicides), insect pests (insecticides) and plant pathogenic fungi (fungicides).



1.2 France uses pesticides on 86% of its cultivated areas, which explains why they are found almost everywhere.

1.3 In the past, certain pesticides such as DDT have accumulated in soils and then in the food chain, with serious impacts on the health of ecosystems and humans.



1.4 Since then, the most persistent pesticides have been banned and today it is required that pesticides must “disappear” (dissipate, be eliminated) from a field within the year of cultivation.

D.D.T.
Dichlorodiphenyltrichloroethane

ClC1(Cl)C(Cl)C2=CC=C(Cl)C=C2C3=CC=CC=C31

BANNED
1970

CHLORDECONE
A.k.a. Kepone

ClC1(Cl)C(Cl)C(Cl)C(Cl)C(Cl)C(Cl)C(Cl)C(Cl)C(Cl)C1

BANNED
1990

ATRAZINE
6-chloro-N-ethyl N'-(1-methylethyl)-
triazine-2,4-diamine

CCN1C=NC(Cl)=N1CN

EU REGULATED
2003

SIMAZINE
6-chloro-N2,N4-diethyl-1,3,5-
triazine-2,4-diamine

CCN1C=NC(Cl)=N1NCC

BANNED
2001

TERBUTRYNE
2-N-tert-butyl-4-N-ethyl-6-
methylsulfanyl-1,3,5-triazine-2,4-diamine

CCN1C=NC(S)N1C(C)(C)C

BANNED
2003

DIURON
A.k.a. DCMU

CC(=O)N(C)C1=CC=C(Cl)C=C1Cl

BANNED
2003

AMINOTRIAZOLE
3-Amino-1,2,4-triazole

NC1=CN=CN1

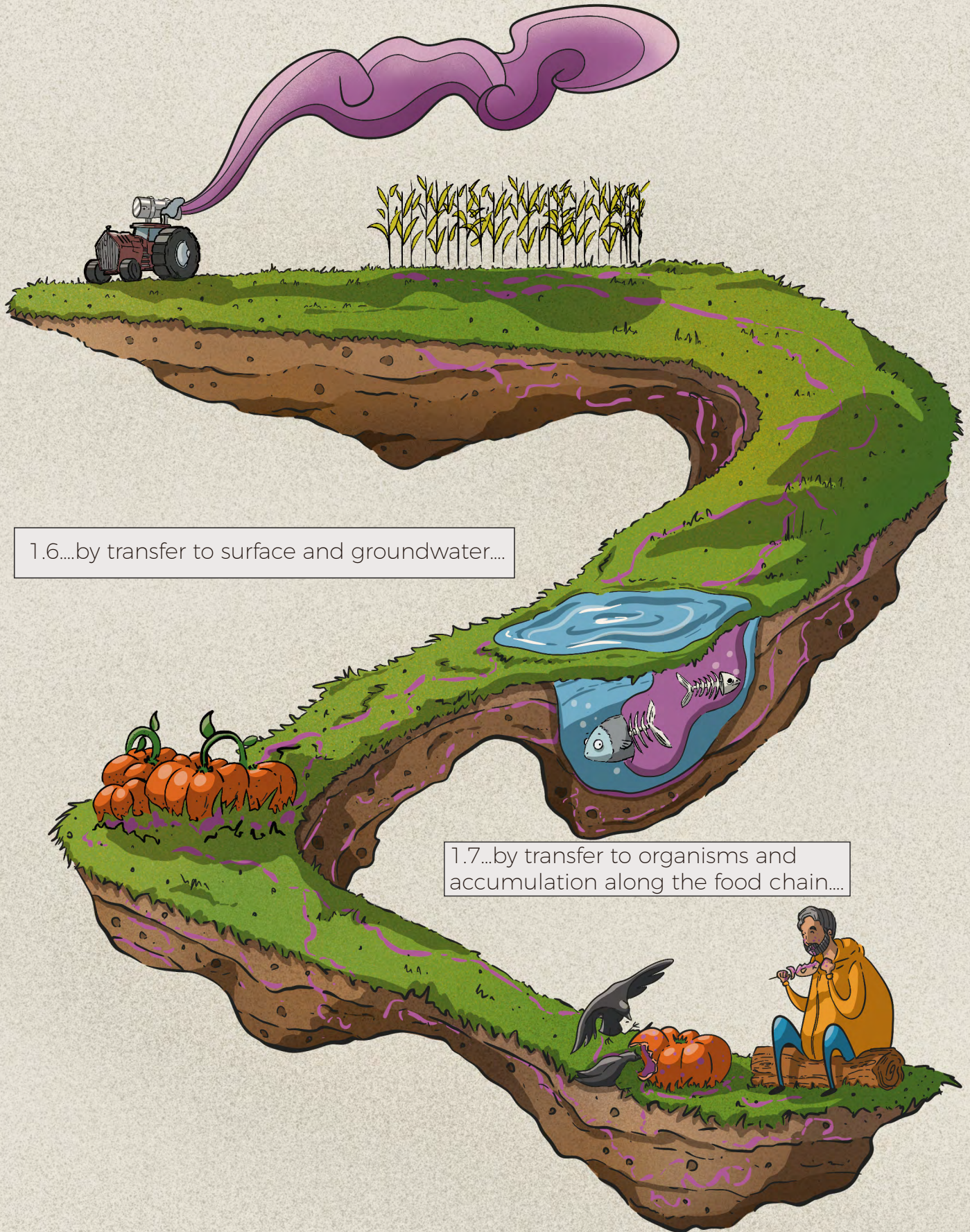
BANNED
????

S-METOLACHLOR
2-chloro-N-(2-ethyl-6-methylphenyl)-N-
[(2S)-1-methoxypropan-2-yl]acetamide

CCOC(=O)N(C)C1=CC=C(C)C=C1Cl

BANNED
????

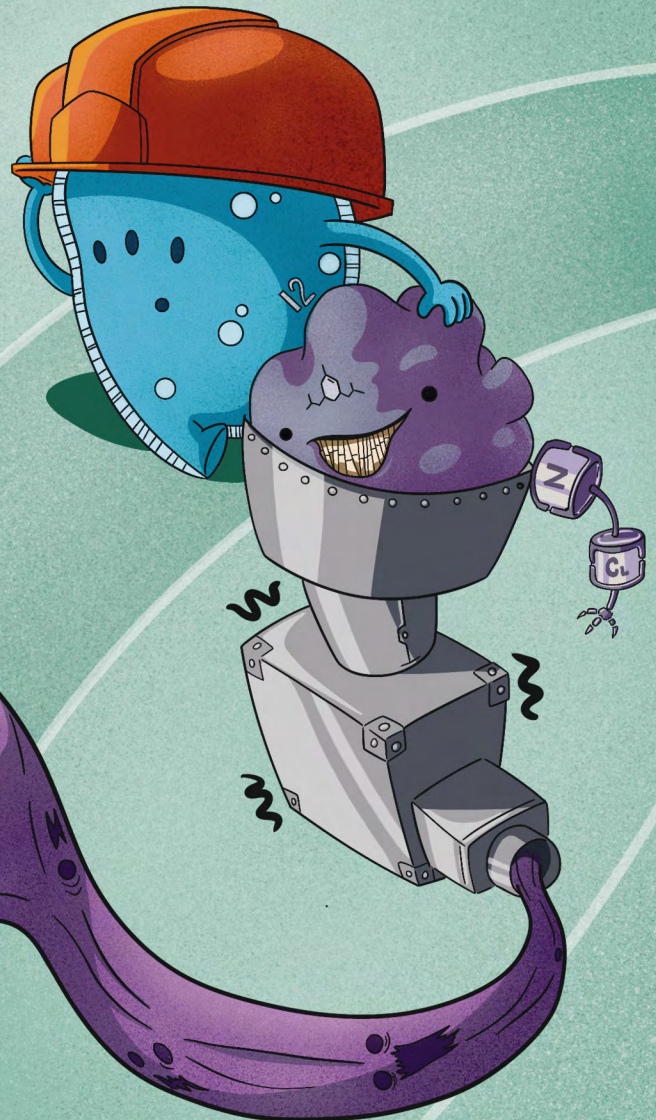
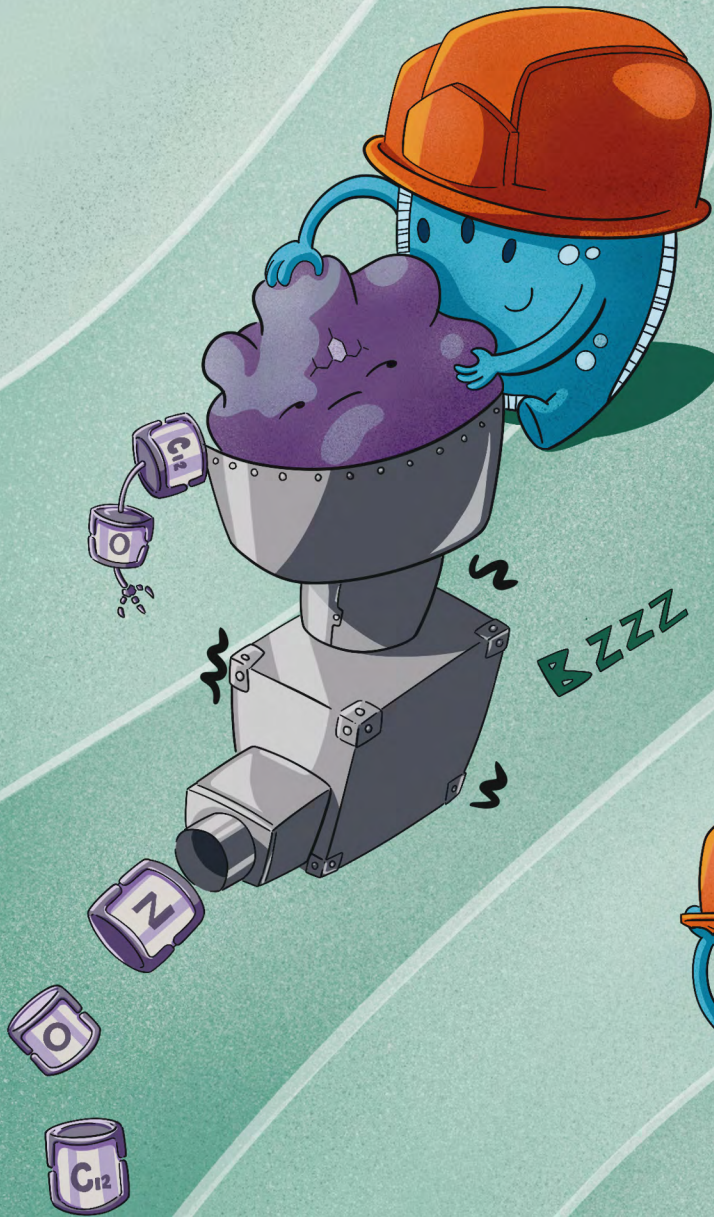
1.5 This dissipation takes place by volatilization, which however only constitutes a dilution of the initial mass of pesticides in the environment....



1.6....by transfer to surface and groundwater....

1.7...by transfer to organisms and accumulation along the food chain....

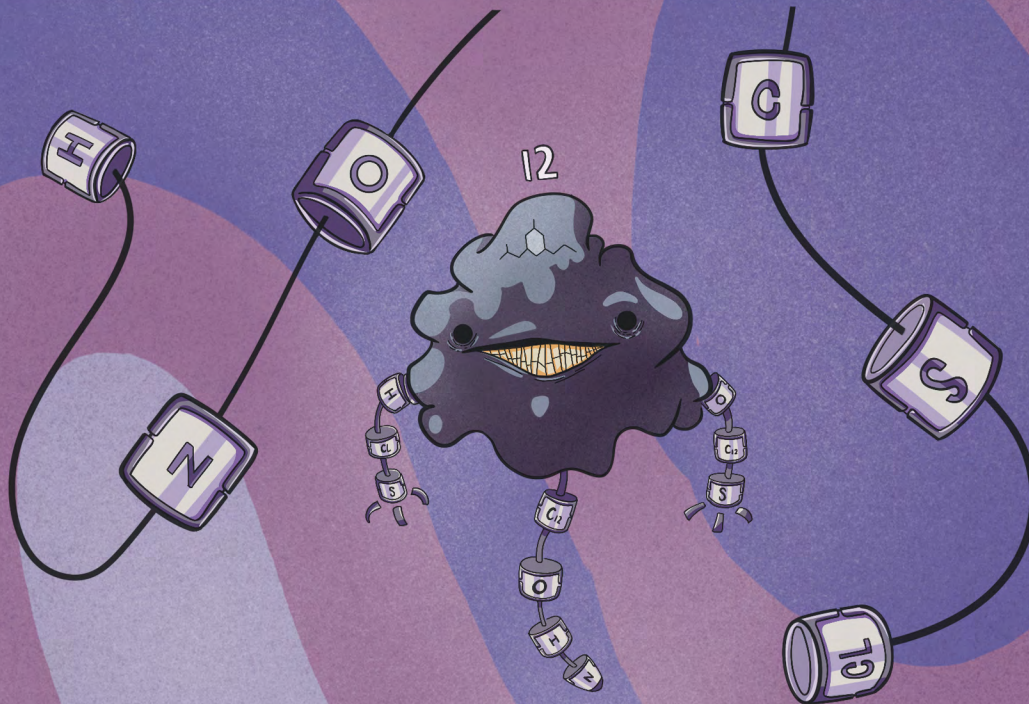
1.8 ...and by degradation. Because no living being wants to breathe or drink pesticides, only degradation is acceptable as a process of elimination.



1.9 Problem: the degradation process can be incomplete and lead to the accumulation of sometimes persistent and harmful transformation products.

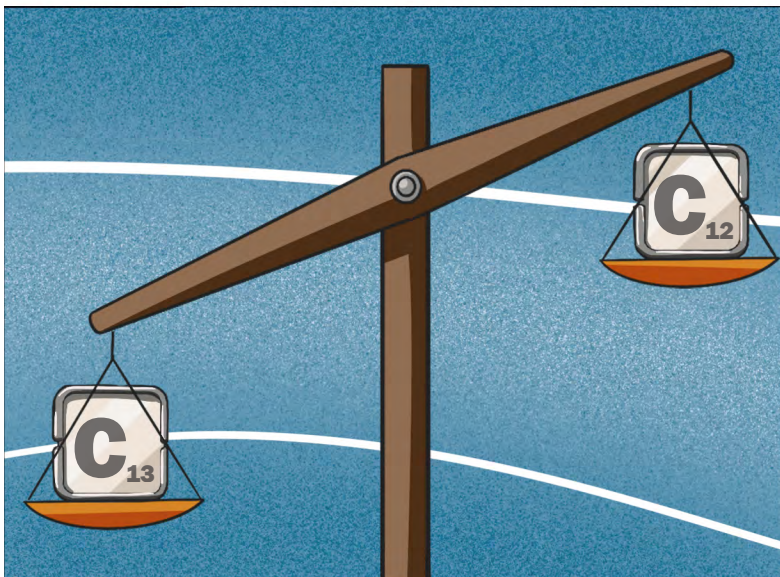


2.1 The project DECISIVE, funded by the French National Research Agency, has developed an innovative approach that demonstrates the existence of pesticide degradation in soils. This approach is based on stable isotopes in pesticides. How does this work?

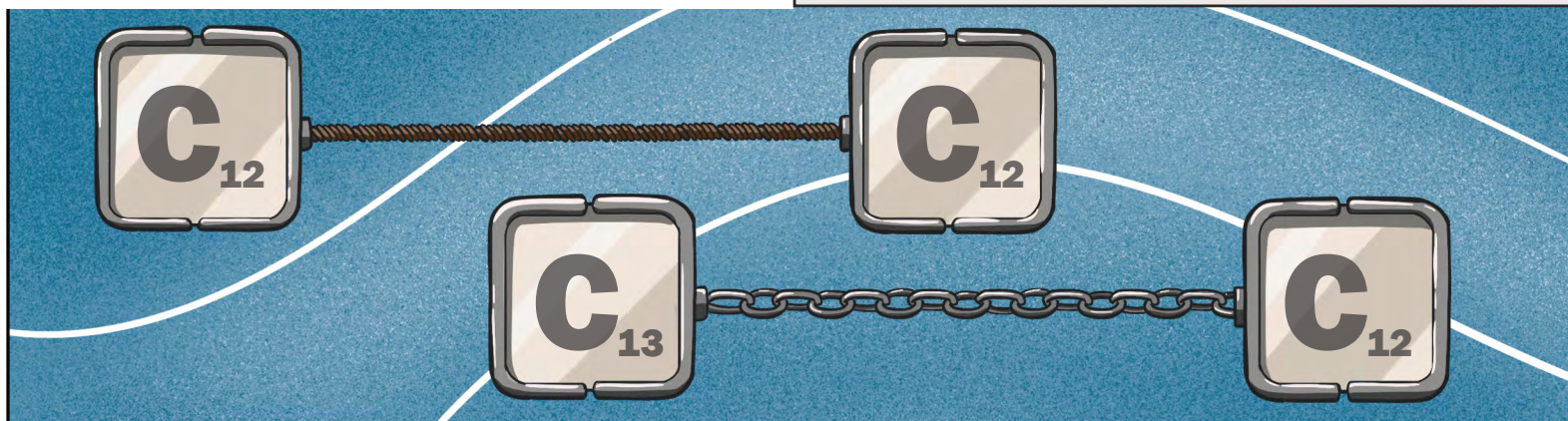


2.2 Pesticides are synthetic molecules made up of the elements carbon (C), hydrogen (H) and oxygen (O), sometimes also containing other elements such as nitrogen (N), sulfur (S) or chlorine (Cl), among others.

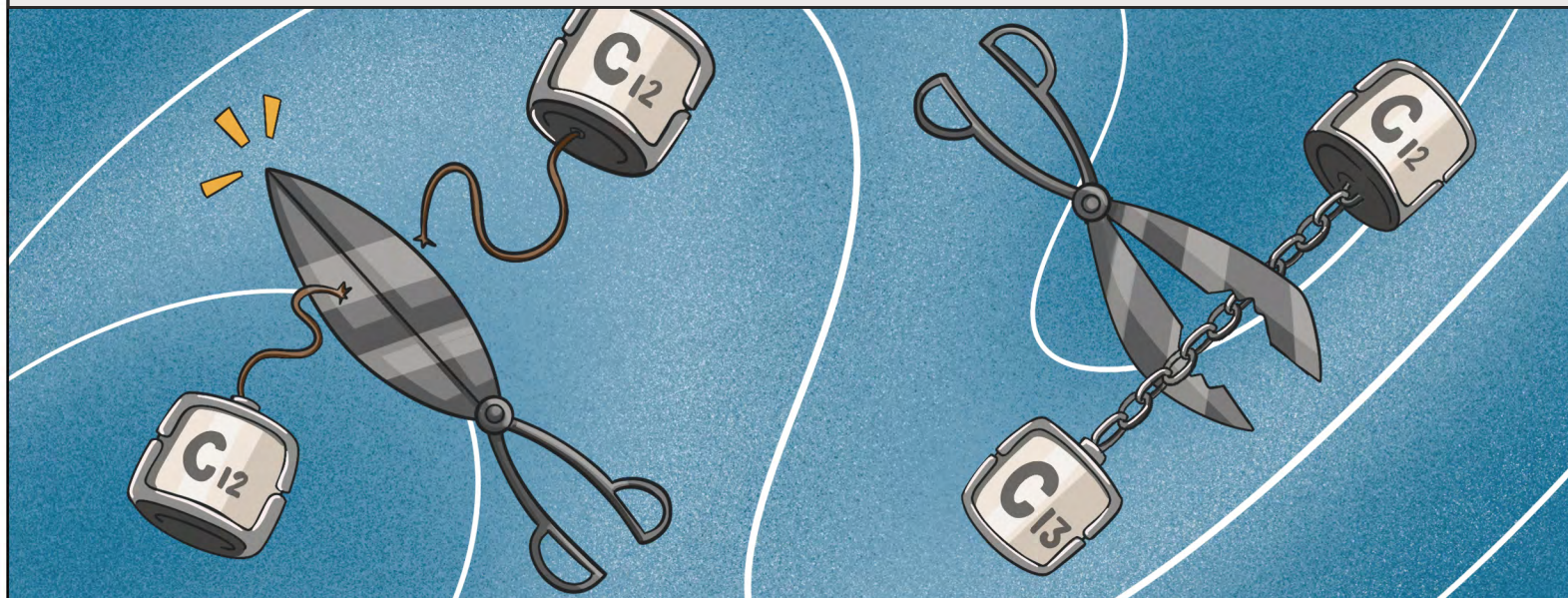
2.3 Most of these elements are present in nature in at least two stable forms, called stable isotopes, which have different masses. But contrary to popular belief, these isotopes are not radioactive and therefore natural and not harmful.



2.4 For carbon, for example, we can observe a light isotope with an atomic mass of 12, which is very abundant on Earth (99%), and a heavier isotope with an atomic mass of 13, a minority (1%).

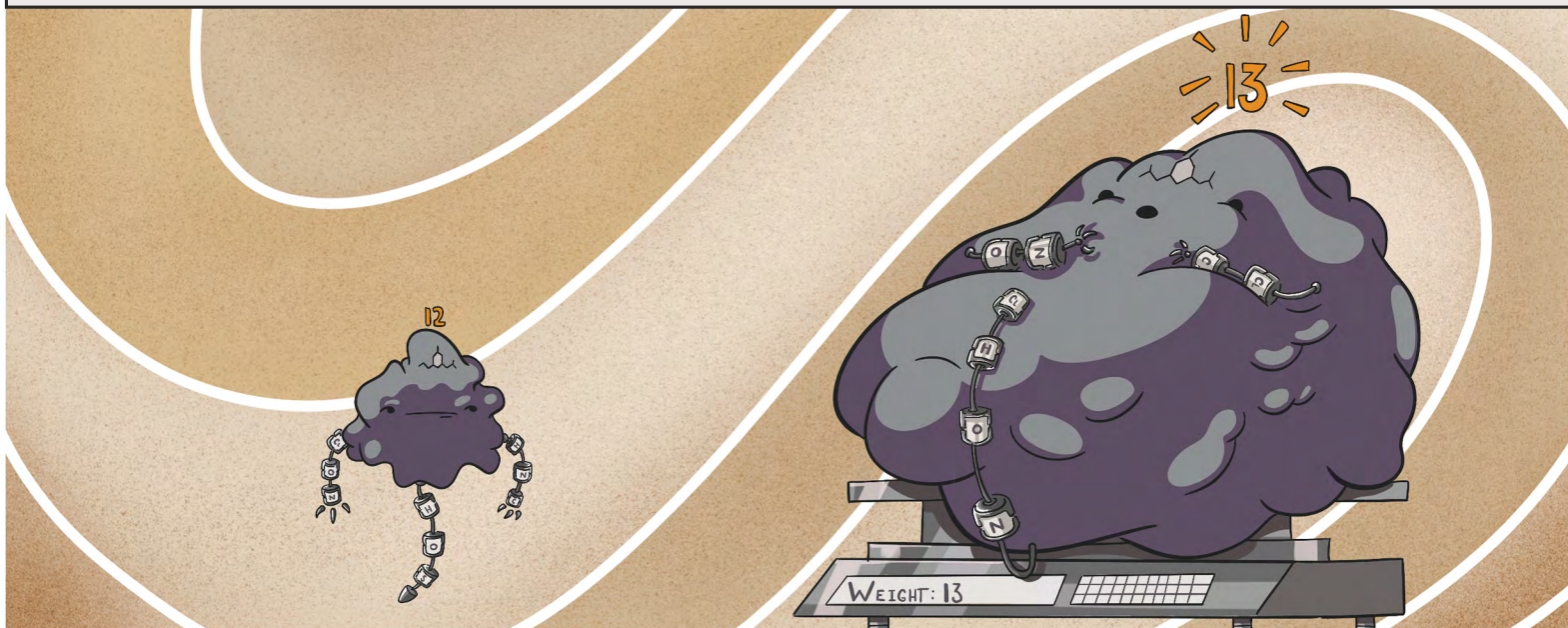


2.5 Chemical bonds in a molecule are generally somewhat more stable when a heavy isotope is part of the bond.

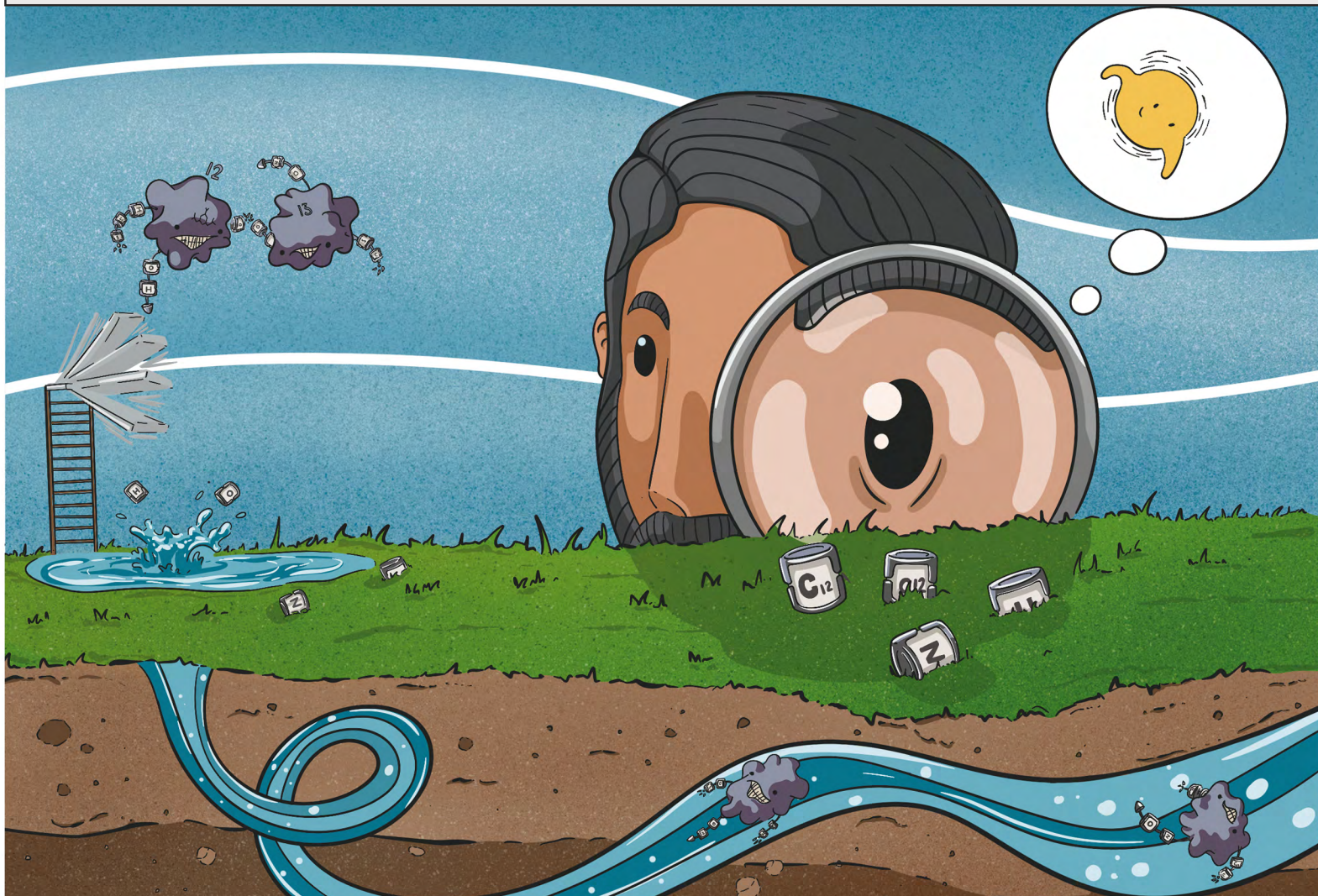


2.6 Degradation processes cause openings of chemical bonds, and as a result pesticides without heavy isotopes (with weaker bonds) degrade slightly faster than pesticides with heavy isotopes (with more stable bonds).

2.7 We will then see that pesticides that are not yet degraded in soil become a little heavier over time. This is called isotopic enrichment. This enrichment can be detected by an isotope mass spectrometer, a device that counts isotopes.

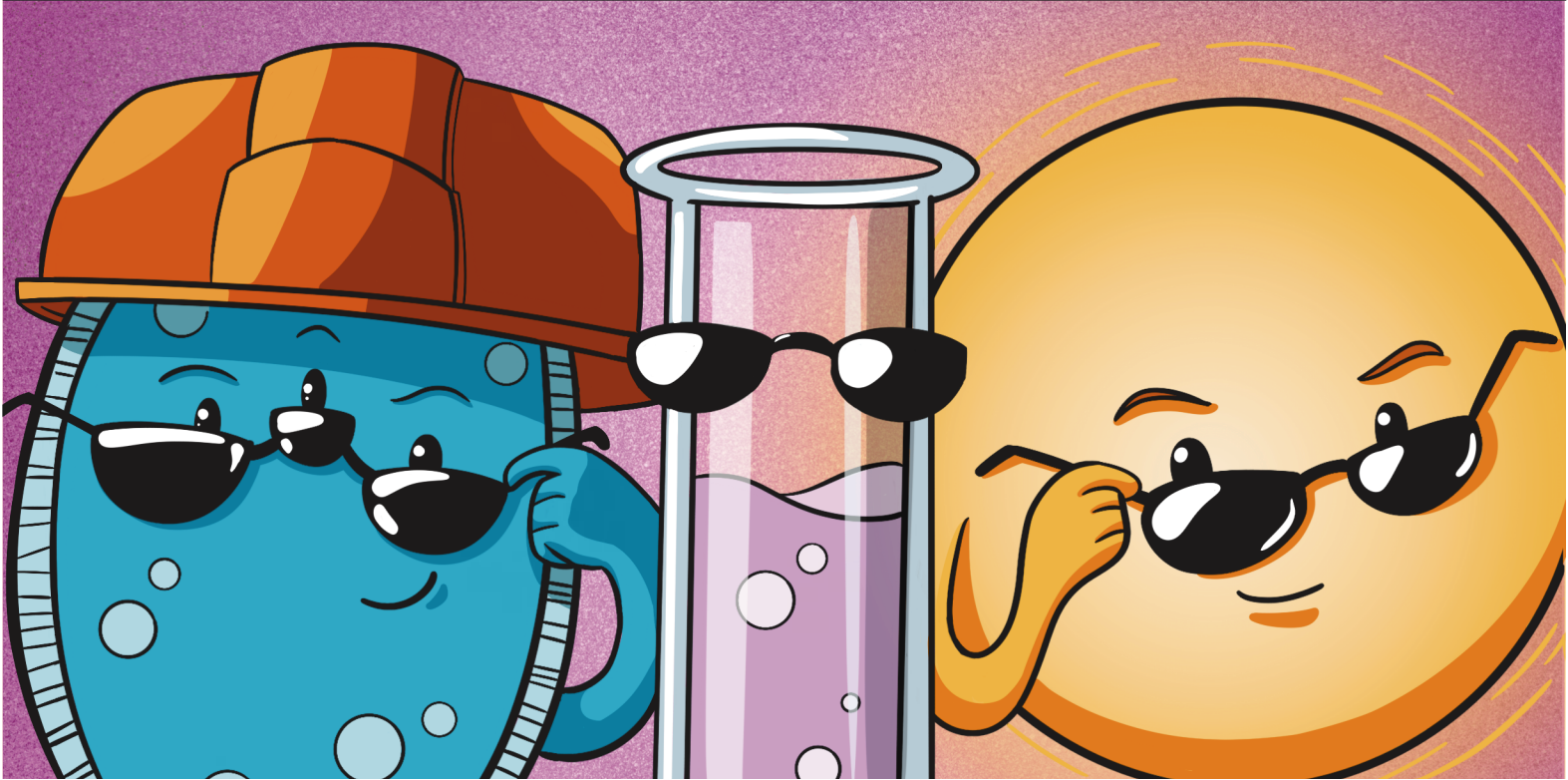


2.8 The volatilization of pesticides and their transfer to water is not accompanied by isotopic enrichment.

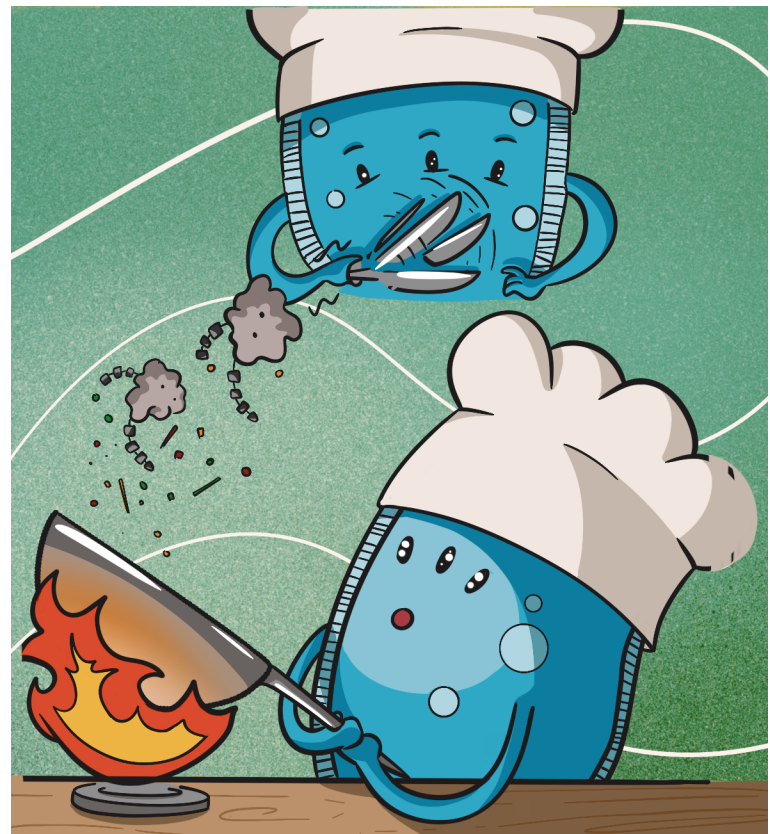
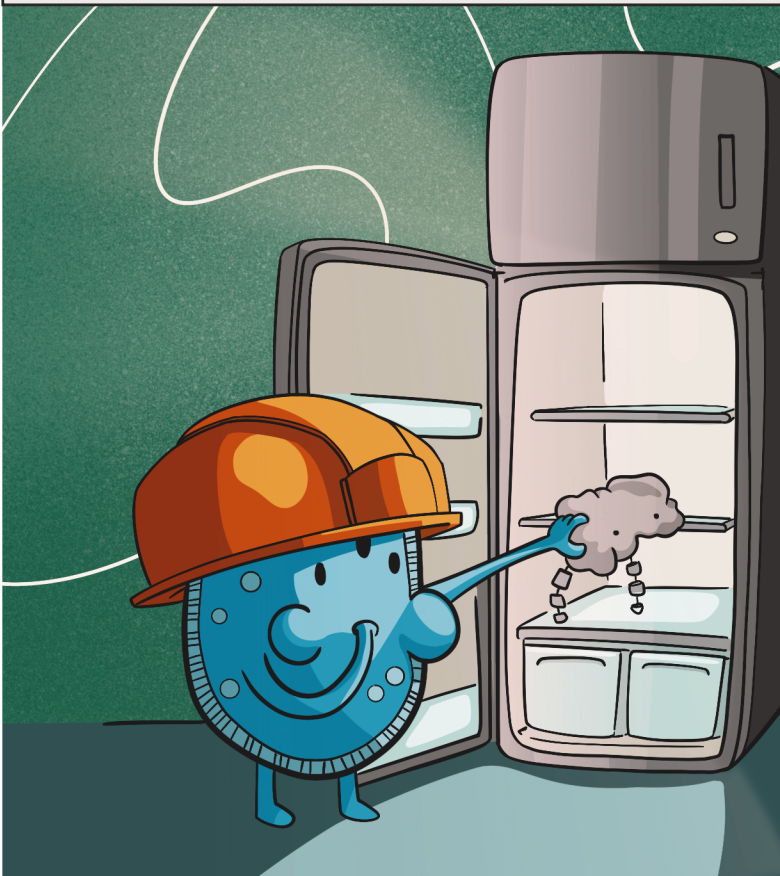


2.9 If isotopic enrichment is measured in a soil, then there is evidence of degradation. In chapter 3, we will explain a little more about the different types of degradation.

3.1 In a field, three types of degradation can be active: biodegradation, abiotic chemical degradation, and photodegradation. It is important to differentiate these processes because the transformation pathways and therefore the transformation products generated are often different.

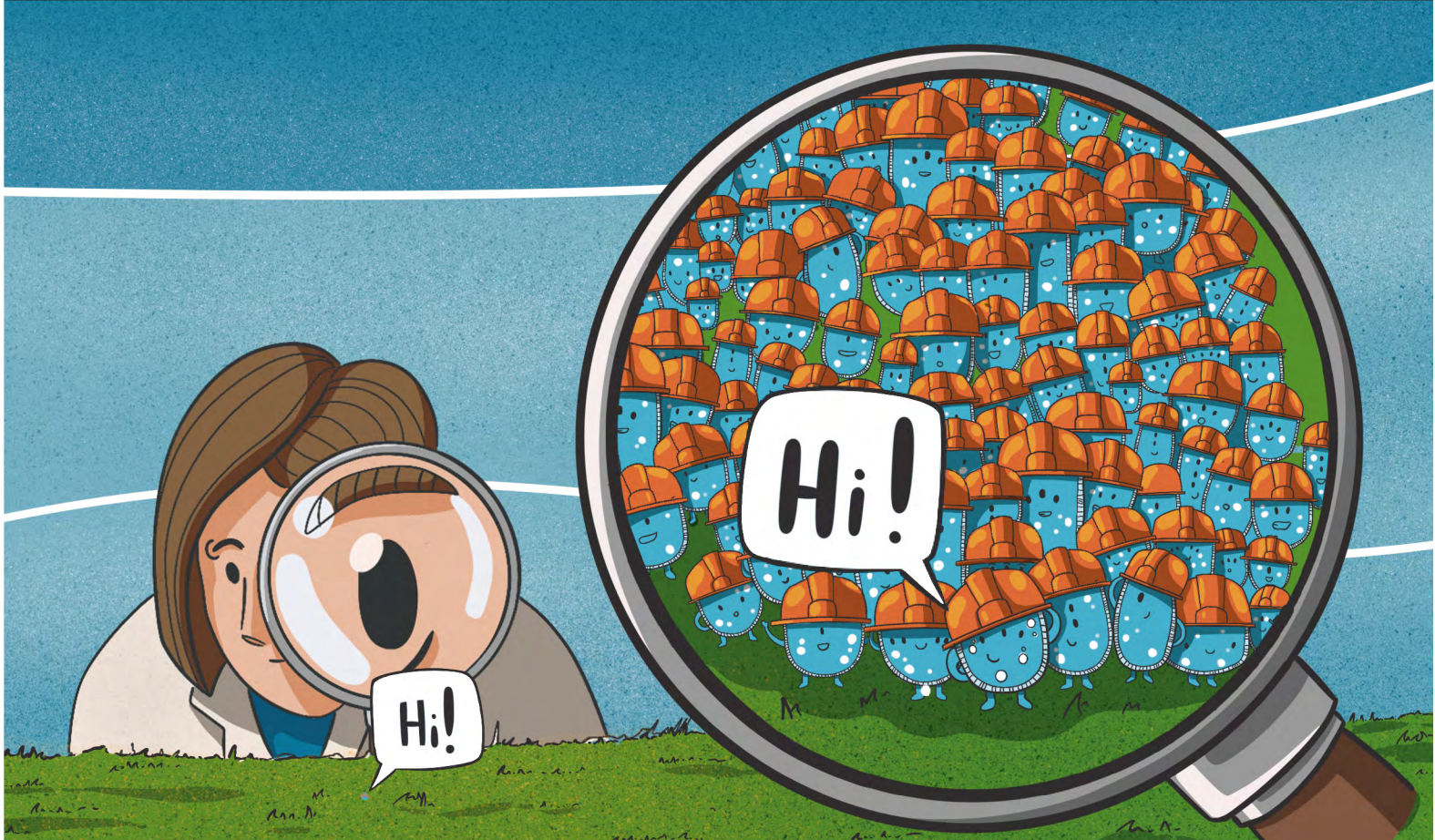


3.2 Biodegradation is mainly done by bacteria either by the co-metabolic route or by the metabolic route. The pesticide is either used as a source of energy and/or a source of nutrients such as nitrogen, sulfur and phosphorus.

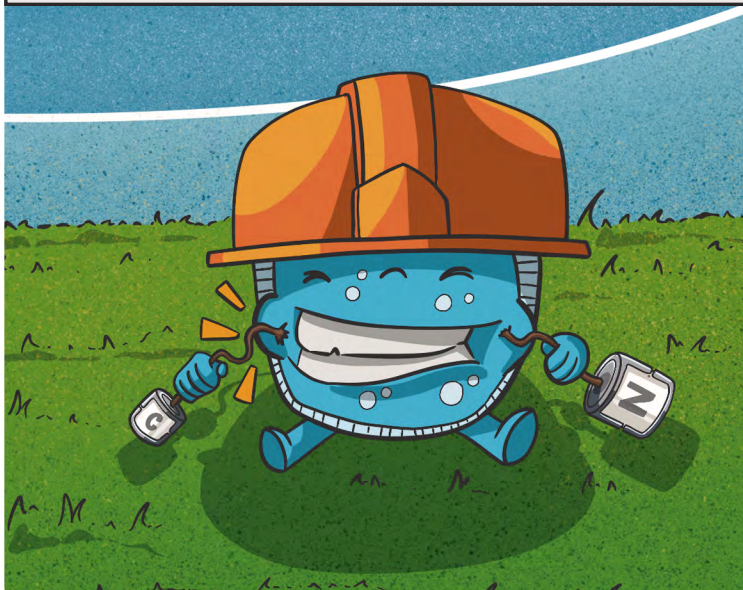


3.3 For this, bacteria must adapt by recruiting genes that encode enzymes. These are proteins that catalyze the stages of degradation. As pesticides are non-natural substances, the adaptation process is sometimes very long to lead to the establishment of biodegradation.

3.4 One gram of soil can host billions of bacteria, and it is unknown how many different species can be found there. There is every chance that among them a population of bacteria can acquire the means to consume the pesticide as a nutrient source for its growth.

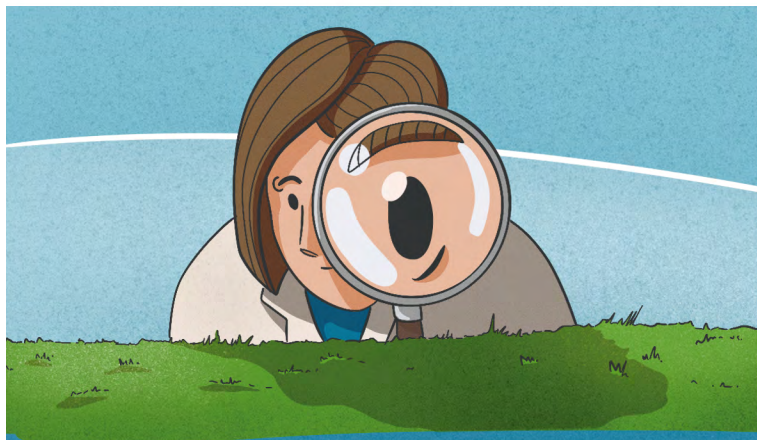


3.5 If all goes well, bacterial biodegradation will proceed and the remaining pesticides in the soil will become enriched in heavy isotopes. This can be observed even for several different elements in the molecule (for example carbon (C-13 versus C-12) and nitrogen (N-15 versus N-14). This is called multi-element isotopic enrichment.

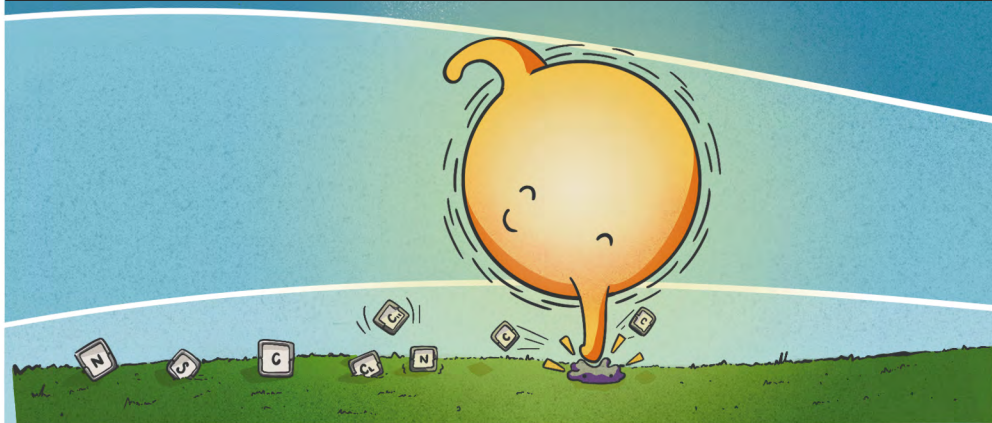


3.6 But sometimes bacteria cannot adapt and create enzymes to break down pesticides. This has been observed for example for certain pesticides having chlorine atoms in their molecule. In this case the pesticides persist and there is no isotopic enrichment linked to biodegradation.

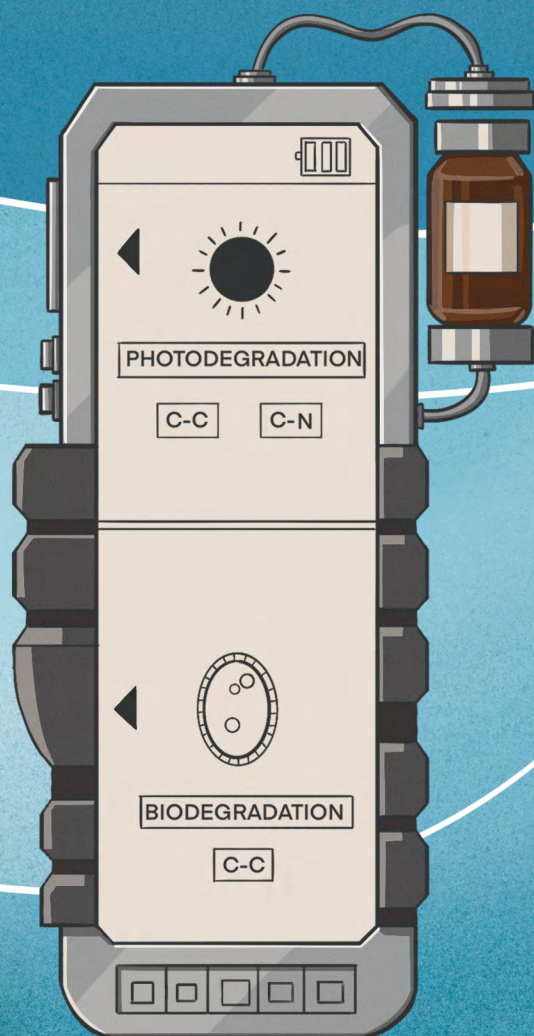
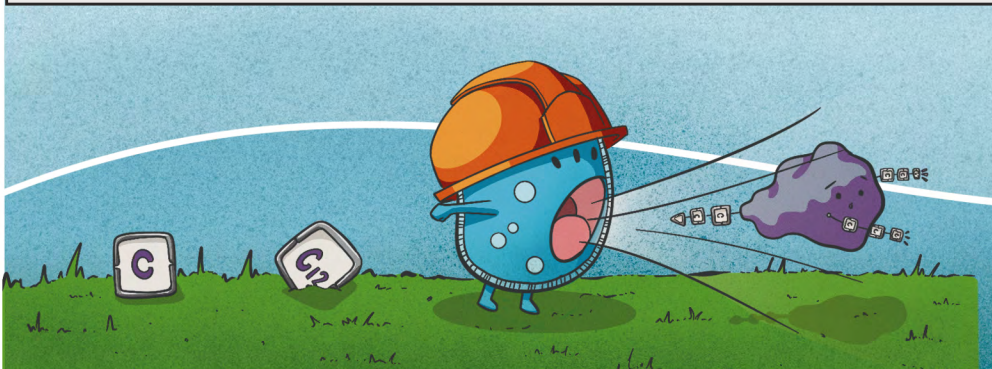
3.7 In this case, depending on the pesticides, but more rarely, abiotic chemical degradation could be the major degradation process in a soil. For example, iron minerals in the soil can react with chlorinated pesticides, this can remove the chlorine atoms from the molecule.



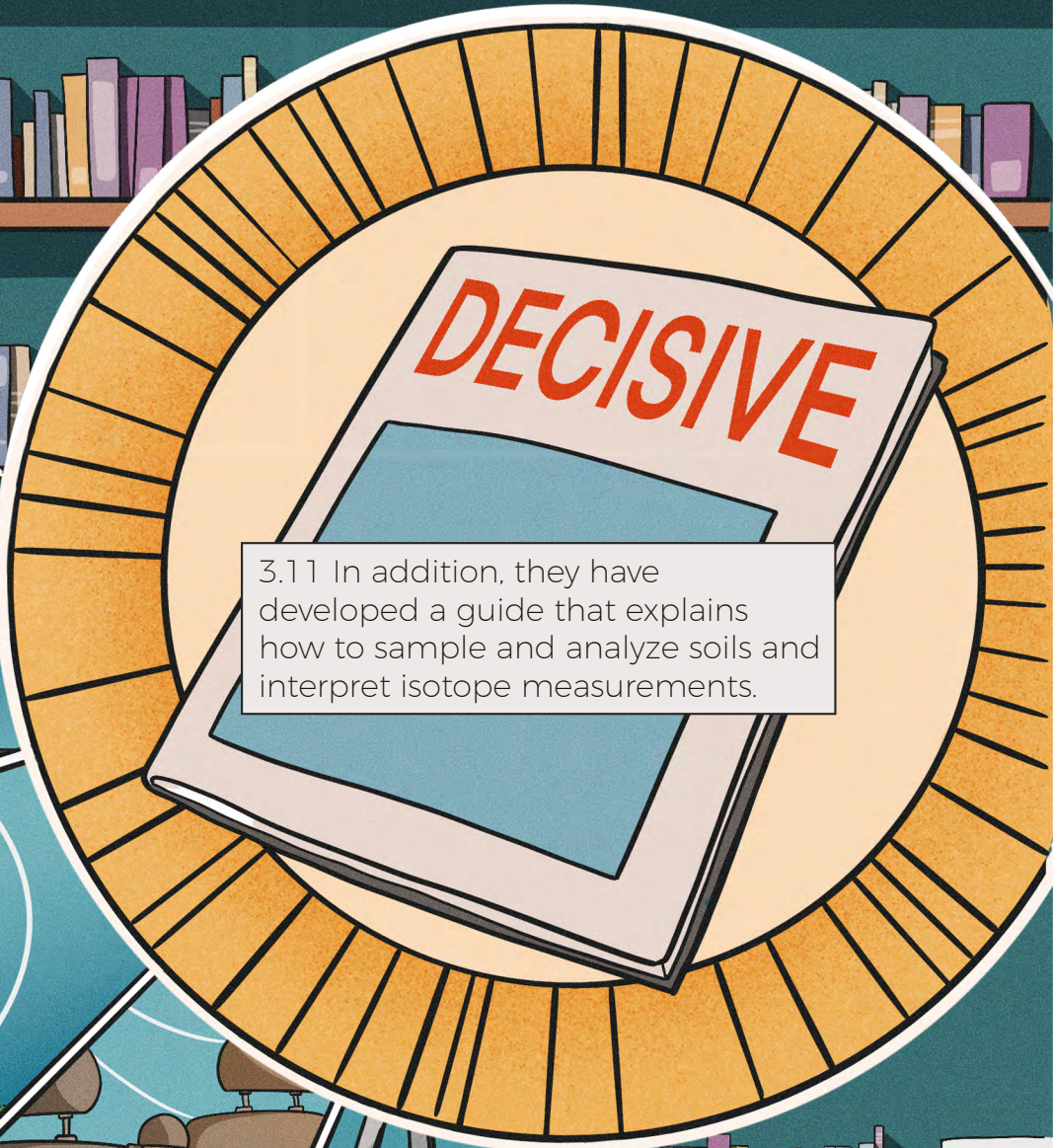
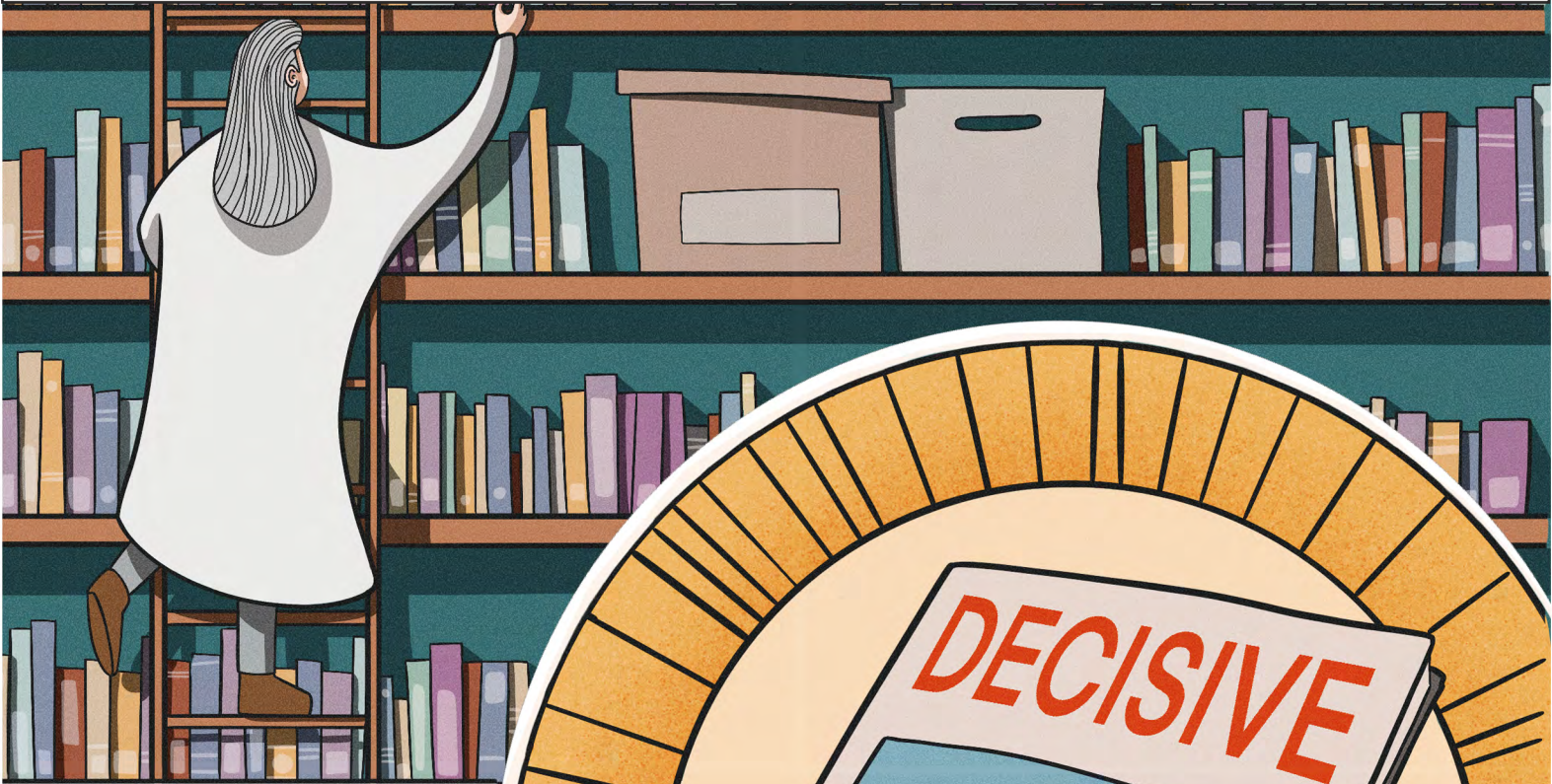
3.8 Abiotic degradation can induce different enrichments compared to biodegradation in the remaining pesticides. For example, carbon enrichment may be created, while nitrogen enrichment could be zero.



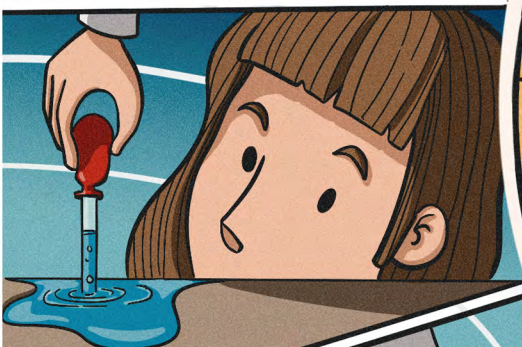
3.9 If this is the case, we can therefore use the isotopic tool to distinguish between biodegradation and abiotic degradation. Or between these two processes and photodegradation, thanks to an even different enrichment.



3.10 DECISIVE researchers have created a database that communicates quantitative information about how each degradation process influences the enrichment of the isotopes of each element.



3.11 In addition, they have developed a guide that explains how to sample and analyze soils and interpret isotope measurements.



DECISIVE



3.12 Thanks to this, we will be able to better understand the fate of pesticides in soils in the future.