

Ammonia goes green

A gentler method of putting nitrogen into the soil is on its way



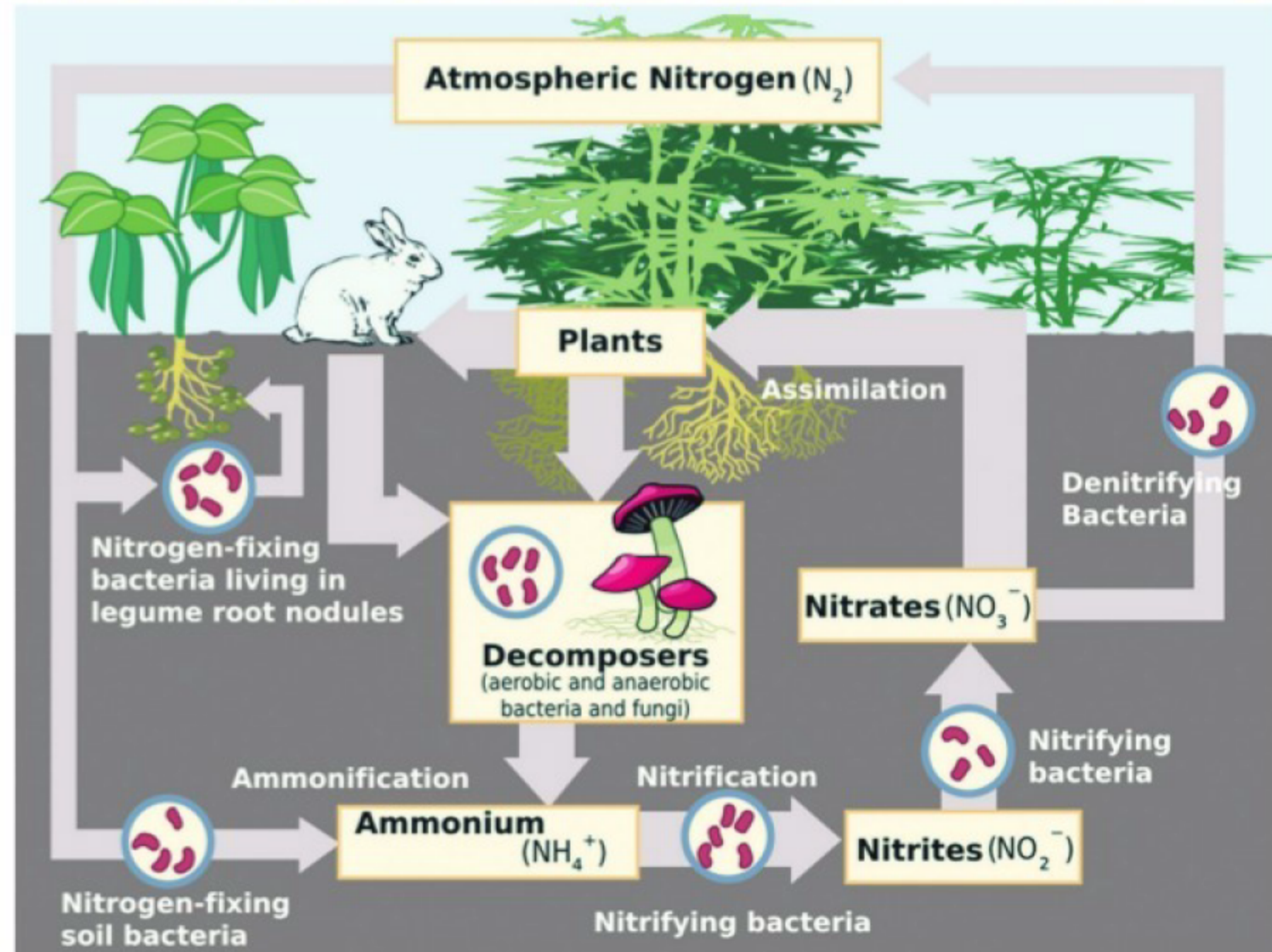
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With world population and pressure on land set to increase, the demands on farm productivity, and hence, the use of chemical fertilisers, will be greater than before. The current means of producing chemical fertilisers, however, uses huge energy and causes huge carbon dioxide emission. The process infamously consumes three per cent of the world's production of natural gas and releases three per cent of the world's carbon emissions.

It is in this context, that Jun Wang, Liang Yu, Lin Hu, Gang Chen, Hongliang Xin and Xiaofeng Feng, from the University of Central Florida and the Virginia Polytechnic Institute and State University, report in the journal, *Nature Communications*, a method of producing ammonia — the raw material for fertilisers — without the high temperature and pressure that the industrial process demands. This may hence be the answer to the world's urgent need to grow more food and yet contain carbon emissions.

Nitrogen is a crucial element in the formation of vegetable tissue. Agriculture hence depends on sufficient nitrogen, in a form that can be used, being there in the soil. During aggressive cultivation, the nitrogen gets consumed faster than it can be restored by natural processes and the land loses fertility. This limiting factor was overcome when ways to manufacture chemicals that pump nitrogen into the soil were found and since then, the production of grain and the production of fertiliser have boomed.

As nitrogen, at 78 per cent, is the most abundant gas in the atmosphere, one would expect that getting it into the soil should be routine. But this is not so as the nitrogen in the air, which is the end product of the nitrogen cycle, is not in the form that can be used. Atmospheric nitrogen consists of molecules where two atoms of nitrogen are very firmly bound together. The strength of this bond does not



allow nitrogen atoms to participate in reactions with other compounds. Before they can be used by processes of plant growth, the bond between the atoms needs to be broken and the nitrogen atoms presented in a less firmly attached form.

Farmers have traditionally used compost, which is decomposed plant matter, or animal refuse, to release "active" nitrogen and fertilise their fields. The ammonia molecule, or NH₃, also has usable nitrogen, and ammonia salts can be added to the soil as powerful fertilisers.

Creating ammonia, or its salts from the nitrogen in the air, in the lab, particularly in quantity, however, was not feasible till the Haber process was

developed in the early 20th century. In this process, intense heat and high pressure, with the help of "helper" agents, or catalysts, get nitrogen atoms to separate and take on three hydrogen atoms in place of their normal partner, to form ammonia. The process, however, is energy intensive.

The reaction, depicted as N₂+3H₂=2NH₃, in fact, is exothermic, or one that gives off heat. This would suggest that the process needs no addition of heat but may benefit from cooling. This, however, is not true because the nitrogen molecule does not separate as two atoms, which can separately combine with hydrogen, unless it is heated to a few thousand degrees centigrade. This is also true to

an extent of the hydrogen molecule. Temperature, in turn, impedes the exothermic reaction, which hence proceeds only under very high pressure. Fortunately, things can be made easier by catalysts, or special substances that provide half-way stops that enable the reaction go through in stages.

The main catalyst in the Haber process is finely divided iron, on the surface of which the molecules loosen up, so that the N and H atoms are able to come in contact. Even so, the temperature needs to be about 550°C and the pressure over 200 atmospheres. As the efficiency of the reaction is about 15 per cent, there have to be several passes before sufficient ammonia is

produced.

Hydrogen gas also needs to be produced, which calls for power and high temperatures too. The whole process is thus energy intensive, fossil-fuel dependent and polluting. However, as it is the best one known for making ammonia at a very large scale, it has been extensively used and agriculture that does not use chemical fertiliser can no longer be viable.

If it is thus essential to have high temperature for turning out ammonia, how is it that natural processes, like microbes in the soil, and some plants, are able to create active nitrogen simply at the ambient temperature? The way nature does it is with the help of enzymes, complex molecules, which, incidentally, contain iron. These depend, not on the brute force method of high temperature, where nitrogen atoms bound in molecules are battered apart, but on the property of the iron atom to gently loosen nitrogen bonds, so that supply of just a little energy can set the atoms free, long enough for them to combine with atoms of other elements.

Discovery of a similar, low temperature process for producing ammonia, using electricity from renewable sources, would be an eco-friendly route to fertilisers, the paper in *Nature Communications* says. As ammonia is also a good energy source and burns without pollution, such a process could be a method of storing and retrieving surplus electric power, the paper says.

The quest for such a method, of course, has been on for decades. The formation of NH₃ from N₂ and H₂O is essentially climbing back to extract N and H from the stable states of N₂ and H₂O. We say "climbing back" because NH₃ readily burns in oxygen to yield nitrogen and water and it is the reverse that needs energy. The approach to low temperature methods to bring this about has hence followed nature's lead and a number of catalysts, based on ruthenium, platinum, gold, iron and nickel have been developed, the paper says.

These catalysts, however, have generally shown low activity. Another concern, the paper says, is that in a water medium, catalysts that promote N₂ dissociation also promote generation of hydrogen gas. This leads to the second process taking place, and the efficiency, for production of NH₃, is less than one per cent. The need is hence for an agent that promotes N₂ dissociation and suppresses hydrogen evolution.

The current study reports encouraging results on using nanoparticles of palladium with a supporting base of carbon black — denoted as Pd/C. When used in a selected medium that suppresses the hydrogen evolution reaction, the catalyst enabled a reasonable level of NH₃ production, needing the application of low electrical energy and with efficiency of 8.2 per cent. Trials using similarly prepared particles of gold and platinum, in place of palladium, showed that these metals were also capable of catalysing the reaction, but with much lower efficiency and less than 10 per cent of the yield.

Enquiry into how palladium turns out to be a unique catalyst for this reaction leads to insight into the mechanism of the action. "Our findings open up an avenue to develop efficient electro catalysts for not only the electro reduction of N₂ to NH₃, but also other challenging electro catalytic reactions for renewable energy conversions," the paper says.

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PLUS POINTS

Deepest evidence



Plastic and other pieces of debris have been found in the deepest parts of the ocean, according to a new study.

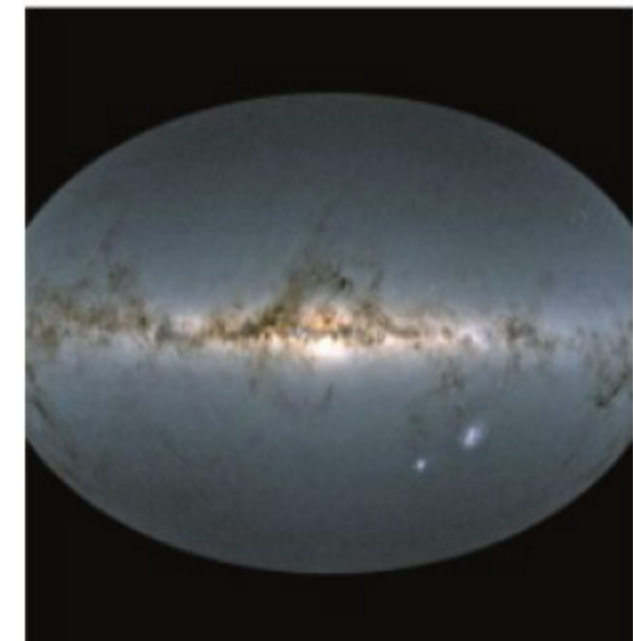
A single-use plastic bag was among the 3,500 fragments discovered at a depth of 10,898 metres. More than one-third of what was found was macroplastic — visible pieces of plastic larger than five mm. Almost 90 per cent of these were single-use plastics, according to the new study produced by the Japan Agency for Marine-Earth Science and Technology.

The research only includes the items that were sitting on the sea floor, not what is floating above it, therefore demonstrating the deepest evidence of the ocean's pollution problem. "As the deep sea is likely to be the final destination of floating plastic debris, the frequent occurrence and widespread distribution of plastic debris in the deep sea, far away from populated coastal areas, indicate that large numbers of plastic debris pieces are distributed throughout the water column and in the high seas," the researchers said.

Nearly 600 pieces of debris that were found had deep-sea organisms interacting with the item — providing further evidence that human pollution was interfering with ocean life. The researchers have called on regulation on the production of single-use plastic to stop the problem becoming worse, the Science Alert website reported.

The Independent

Milky Way mapped



Last month, astronomers in Europe released a three-dimensional map of the Milky Way. It is the most detailed survey ever produced of our home galaxy. It contains the vital statistics of some 1.3 billion stars — about one per cent of the entire cosmic panoply of which Earth and the Sun are part. Not to mention measurements of almost half a million quasars, asteroids and other flecks in the night.

Analysing all these motions and distances, astronomers say, could provide clues to the nature of dark matter. The gravity of that mysterious substance is said to pervade space and sculpt the arrangements of visible matter. Gaia's data could also reveal information about the history of other forces and influences on our neighbourhood in the void. And it could lead to a more precise measurement of a historically troublesome parameter called the Hubble constant, which describes how fast the universe is expanding.

The map is the latest result from the European Space Agency's Gaia mission, which was launched into an orbit around the Sun in December 2013. It was built by an international collaboration of European astronomers and universities as the successor to the Hipparcos satellite, which charted the positions of about two million stars. Gaia's cameras find the distances to stars by triangulation, measuring how their images shift against background stars and quasars as the spacecraft swings from one side of its orbit to the other — a baseline of about 186 million miles. A preliminary data release, containing information on two million stars, was published in 2016.

The new data set is based on 22 months, from July 2014 to May 2016, of staring at the sky. The first sifting of these stars has led to new insights into the types and colours and ages of the stars, and has allowed astronomers to distinguish subsets of stars with different histories and origins in the galaxy, which could lead to a better account of how and when the Milky Way formed.

The mission continues. The final Gaia catalogue, expected in the early 2020s, will include positions, motions, brightnesses and other parameters of more than one billion more stars. "Gaia is astronomy at its finest," says Fred Jansen, of ESA, the mission's manager.

The Independent

Inside the genome

Here's a look at the process of DNA renaturation that led to the discovery of repeated sequences in DNA

TAPAN KUMAR MAITRA

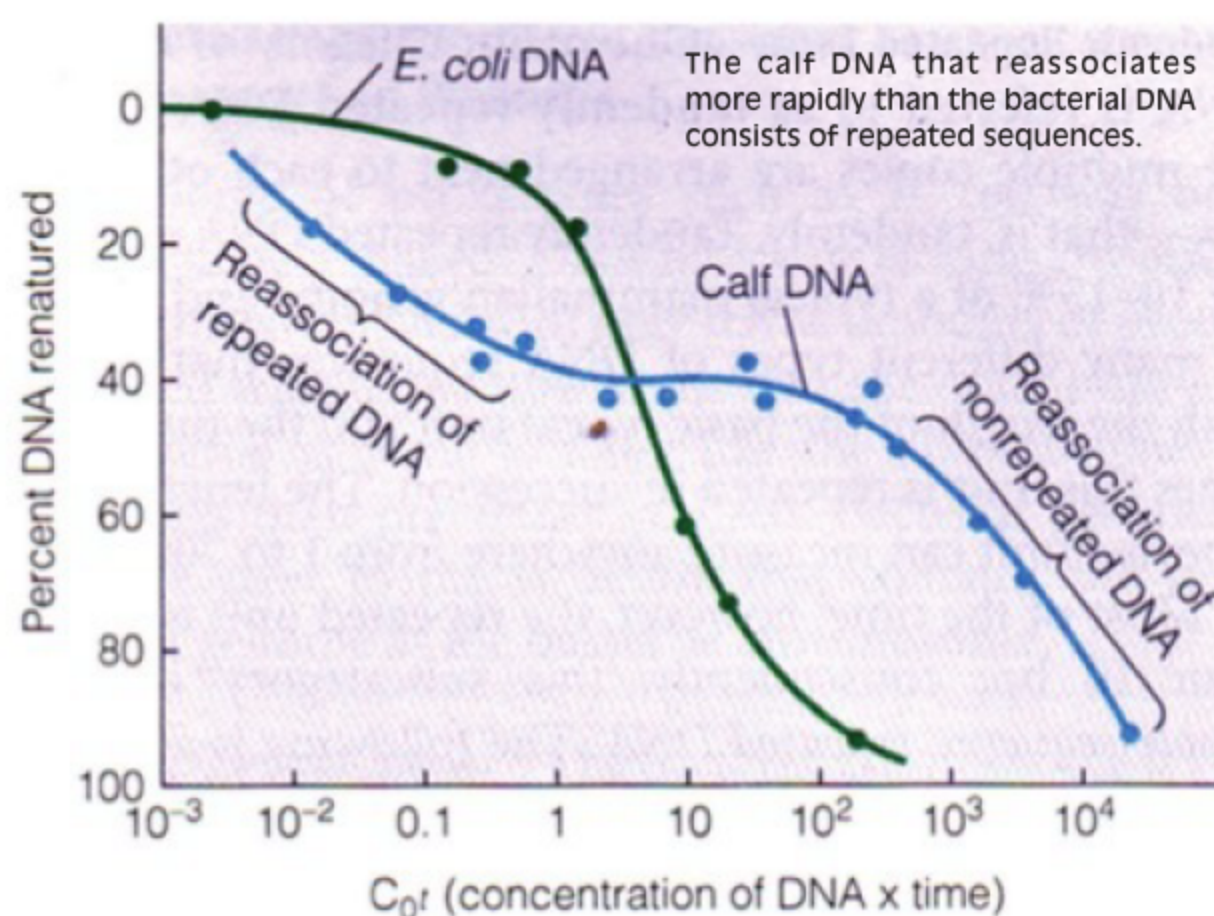
The enormous size of the human genome raises a more fundamental question — is the large amount of DNA found in the cells of humans and other higher eukaryotes simply a reflection of the need for thousands of times more genes than are present in bacterial cells, or are other factors at play as well? A major breakthrough in answering this question occurred in the late 1960s, when DNA renaturation studies carried out by Roy Britten and David Kohne led to the discovery of repeated sequences in DNA.

In the Britten and Kohne experiments, DNA was broken into small fragments and dissociated into single strands by heating. The temperature was then lowered to permit the single-stranded fragments to renature. The rate of renaturation depends on the concentration of each individual kind of DNA sequence; the higher the concentration of any given kind of DNA sequence in the sample, the greater the probability that it will randomly collide with a complementary strand with which it can reassociate.

How would the renaturation properties of different kinds of DNA be

expected to compare? As an example, let us consider DNA derived from a bacterial cell and from a typical mammalian cell containing a thousand-fold more DNA. If this difference in DNA content reflects a thousand-fold difference in the kinds of DNA sequences present, then bacterial DNA should renature 1,000 times faster than mammalian DNA. The rationale underlying this prediction is that any particular DNA sequence should be present in a thousand-fold lower concentration in the mammalian DNA sample because there are a thousand times more kinds of sequences present, and so each individual sequence represents a smaller fraction of the total population of sequences.

When studies comparing the renaturation rates of mammalian and bacterial DNA were actually performed by Britten and Kohne, the results were not exactly as expected. The data obtained for calf and *E. coli* DNA renaturation is plotted as a function of the starting DNA concentration multiplied by the elapsed time. This parameter of DNA concentration X time, or C₀t, is employed in place of time alone because it permits direct comparison of data obtained from reactions run at different DNA concentrations.



When graphed this way, the data reveal that calf DNA consists of two classes of sequences that renature at markedly different rates. One type of sequence, which accounts for about 40 per cent of the calf DNA, renatures more rapidly — at a lower C₀t value — than bacterial DNA. The most straightforward explanation for this unexpected result is that calf DNA contains repeated DNA sequences that are present in multiple copies. The existence of multiple copies increases the relative concentration of such sequences, thereby generating more collisions and a faster rate of re-association than would be expected if each sequence were present in only a single copy.

The remaining 60 per cent of the

calf DNA renatures about a thousand times more slowly than *E. coli* DNA, which is the behaviour expected of sequences present as single copies. This fraction is therefore called non-repeated DNA to distinguish it from the repeated sequences that renature more quickly. Non-repeated DNA sequences are each present in one copy per genome. Most protein-coding genes consist of non-repeated DNA, although this does not mean that all non-repeated DNA codes for proteins.

In bacterial cells virtually all the DNA is non-repeated, whereas eukaryotes exhibit a large variation in the relative proportion of repeated and non-repeated sequences. This provides an explanation, at least in part, for the mystery of the seemingly

excess amount of DNA in species such as Trillium. This organism contains a relatively high proportion of repeated DNA sequences. Using the sequencing techniques described earlier, researchers have been able to determine the base sequences of various types of repeated DNAs and to classify them into two main categories — tandemly repeated DNA and interspersed repeated DNA.

One major category of repeated DNA is referred to as tandemly repeated DNA because the multiple copies are arranged next to each other in a row — that is, tandemly. Tandemly repeated DNA accounts for 10 to 15 per cent of a typical mammalian genome and consists of many different types of DNA sequences that vary in both the length of the basic repeat unit and the number of times this unit is repeated in succession. The length of the repeated unit can measure anywhere from one to 2,000 bp or so.

The second main category of repeated sequence DNA is interspersed repeated DNA. Rather than being clustered in tandem arrangements, the repeated units of this type of DNA are scattered around the genome. A single unit tends to be hundreds or even thousands of base pairs long and its dispersed "copies", which may number in the hundreds of thousands, are similar but usually not identical to each other. Interspersed repeated DNA makes up 25 to 40 per cent of most mammalian genomes.

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