



News and opinions

Nano-pesticides: A great challenge for biodiversity?

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ABSTRACT

Problems such as food shortages in the world, serious soil nutrient loss, and residues of pesticides in the environment have put enormous pressure on humans and the environment. In order to improve the yield and quality of food and alleviate the pressure of traditional pesticides on the environment, nano-pesticides have appeared and have been widely used due to their great role in saving agricultural costs, increasing the output of agricultural products, improving the nutrition and shelf life of foods, and achieving precision agriculture. However, the impact of nano-pesticides on biodiversity is still lacking clear research. We discuss here whether the use of nano-pesticides is a great challenge for biodiversity.

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Introduction

In recent years, with the rapid development of nanotechnology [1–5] and the increasingly prominent problems of food shortages and pesticide pollution in the world [6–10], nano-pesticides have become a hot research topic. Nano-pesticides are a new and more efficient pesticide product which mainly refer to the following two types of pesticides. The first type of nano-pesticides refers to pesticides whose effective ingredients are nano-sized. This kind of pesticides usually include powder pesticides and nano dispersant/(micro) emulsion pesticides [11–13]. The second type of nano-pesticides refers to the pesticides that are loaded with nanomaterials or doped in nanomaterials, or directly coated with nanomaterials to put a “nano-coat” on their surface. Nano-components in this kind of pesticides usually have the functions of improving the performance of efficient components of original pesticides, targeting transportation, protecting pesticides and controlling the release of pesticides [14–20]. Nano-pesticides exhibited advantages over traditional pesticides such as low-volume usage and high efficiency. Traditional pesticides have coarse drug carrier particles, poor dispersibility, poor stability and low biological

activity, and their utilization rate for targeted crops is less than 30% [21–24]. However, for nano-pesticides, the smaller the particle size of nano-pesticides is, the more evenly they are distributed on crop leaves, and the higher their efficacy is. In addition, the nano-carriers of pesticides can not only improve pesticides' dispersibility and stability, but also facilitate the effective ingredients of pesticides to the targeted organisms so as to improve their bioavailability [20,25–29]. These advantages could make up for the shortcomings of large dosage and low efficiency of traditional pesticides in practical applications. Therefore, nano-pesticides have been widely applied. For example, the “Diyarex Gold” nano-pesticide developed using nanotechnology is now on the market. It is used as an antiseptic against powdery mildew and rust of various plants [30]. Conventional glyphosate herbicides have also been developed into nanoemulsions to improve weeding efficiency [12]. Metal nanoparticles are also commonly used as pesticides to control plant diseases and insect pests. Among them, copper nanoparticles are commonly used as fungicides to control fruit tree' diseases [31], and silver nanoparticles are also commonly used as agents to resist plant fungal pathogens [32–34]. However, research on the environmental risks of nano-pesticides is still far behind the development of their application. Considering the persistence, high durability or reactivity of certain nano-pesticides, the combined toxicity of nanomaterials and pesticide [35], and the connectivity of the entire ecosystem [36–38], we believe that nano-pesticides could have a significant impact on biodiversity.

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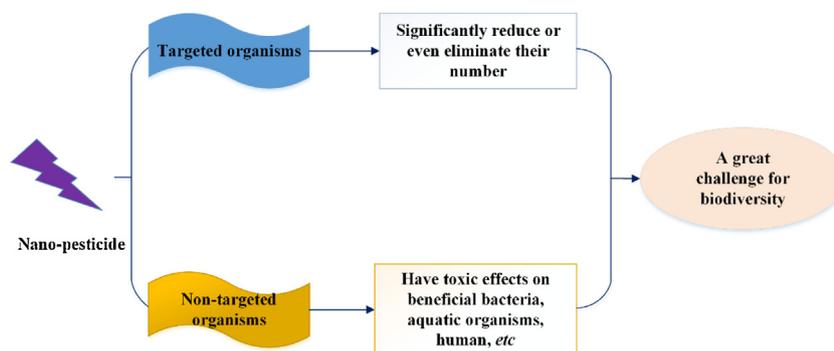


Fig. 1. Nano-pesticides may be a great challenge for biodiversity.

Nano-pesticides for the control of targeted organisms

There is no doubt that nano-pesticides could significantly reduce or even eliminate the number of targeted organisms [29,39–42]. Nano-imidacloprid generally refers to the imidacloprid pesticides wrapped in nano-coat [43,44]. Common imidacloprid pesticides can specifically block the micro-energy neural pathway of pests, so as to achieve the purpose of insecticidal [45–47]. For the effective components of imidacloprid, the nano-coat can protect it from the influence of external factors, improve its biological activity and control its release, thus greatly improving the insecticidal effect of imidacloprid [43,44,48]. At present, nano-imidacloprid is widely used to control *rice planthoppers*, *aphids* and other sucking insects [49]. Studies have shown that nano-imidacloprid is significantly more toxic to *Martianus dermestoides* that of adult stage than general pesticides [40]. Nano-silica is a kind of ultrafine inorganic material with particle size ranging from 1 to 100 nm, due to its small size effect, surface effect and macroscopic quantum tunneling effect, it exhibits many unique properties and is widely used in catalysis, light absorption, medicine and other fields [50–54]. In addition, the toxic effect of nano-silica on insects and microorganisms also leads to the gradual expansion of its application in the field of pesticides [55]. The experiment showed that nano-silica could significantly reduce the amount of *Spodoptera littoralis* [41]. Paulraja et al. [42] prepared a kind of nano chitosan and combined this kind nano chitosan with a botanical pesticide PONNEEM® by using tripolyphosphate and glutaraldehyde as crosslinking agent, and then they got the CSNs - the TPP - PONNEEM compound nano-pesticide. They found that when the CSNs TPP - PONNEEM' concentration in aqueous solution was 0.3%, 90.2% of targeted creatures can be killed. The effect of this nano-pesticide is much higher than ordinary PONNEEM®.

The harm of nano-pesticides to non-targeted organisms

Although the utilization rate of nano-pesticides has been greatly improved compared with traditional pesticides [56–58], there are still about 60% of nano-pesticides cannot act on targeted organisms [59]. In addition, most of the emulsifiable concentrates and microemulsions used in nano-pesticides are polar solvents such as benzenes, alcohols and ketones, which have high acute toxicity and easily find their way into the farmland and groundwater [60–63]. Polar solvents entering the environment are not easy to degrade and will accumulate in the environment, which could widely cause acute poisoning and even death of animals [64–66]. Considering that the nano-pesticides have smaller size, stronger penetrating power to cells, and easier access to targeted microorganisms than conventional pesticides, we have to put forward the following doubts: Compared with common pesticides, are nano-pesticides scattered in the environment more likely to enter

non-targeted organisms and have unpredictable consequences for the non-targeted organisms? In the agricultural production process, nano-TiO₂ pesticides can kill beneficial bacteria while killing harmful bacteria [67]. In addition, while killing targeted organisms, green-synthesized CdS nano-pesticides can also kill a large number of non-targeted aquatic organisms such as river crabs [39]. Undoubtedly, harmful substances of nano-pesticides remaining in edible plants and animals are likely to enter the human body through the food chain and thus endanger human health.

The combined toxicity of nanomaterials and pesticides is unclear

Finally, what combined toxicity of nanomaterials and pesticides can produce and what effects of these combined toxicity have on organisms are still poorly studied. Thus we have to raise concerns about this issue, because its potential impact on the environment and humans is far-reaching.

Conclusion

Based on the above statements, we are very concerned that nano-pesticides could have an unavoidable impact on biodiversity (Fig. 1).

While developing nanotechnology and agricultural technology, we should consider the impacts of these technologies on the entire ecology. At present, the risk assessment procedures of traditional pesticides cannot make a reasonable and comprehensive assessment of the environmental risks of nano-pesticides. Because the nano components contained in nano-pesticides are extremely small, and the additives in nano-pesticides which do not exist in common pesticides are generally highly toxic. In addition, the combined toxicity of nanomaterials and common pesticide ingredients is also very complicated. The environmental risk assessment procedure of nano-pesticides needs to be established urgently.

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References

- [1] M. Chen, S. Zhou, Y. Zhu, Y. Sun, G. Zeng, C. Yang, P. Xu, M. Yan, Z. Liu, W. Zhang, *Chemosphere* 206 (2018) 255–264.
- [2] M. Chen, X. Qin, G. Zeng, *Nano Today* 17 (2017) 11–13.
- [3] M. Chen, X. Qin, G. Zeng, *Trends Biotechnol.* 35 (2017) 836–846.
- [4] S. Kang, Y. Zhu, M. Chen, G. Zeng, C. Zhang, P. Xu, *Nano Today* (2019), <http://dx.doi.org/10.1016/j.nantod.2019.1001.1001>.
- [5] M. Chen, Y. Sun, J. Liang, G. Zeng, Z. Li, L. Tang, Y. Zhu, D. Jiang, B. Song, *Environ. Int.* 126 (2019) 690–698.
- [6] X. Qi, Y. Fu, R.Y. Wang, C.N. Ng, H. Dang, Y. He, *Appl. Geogr.* 90 (2018) 214–223.
- [7] E. Arevalo, S. Panserat, I. Seiliez, A. Larrañaga, A. Bardonnat, *J. Fish Biol.* 92 (2018) 642–652.
- [8] M. Chattopadhyay, S.K. Mitra, *Theor. Appl. Climatol.* 131 (2016) 523–530.
- [9] M. Sole, M. Bonsignore, G. Rivera-Ingraham, R. Freitas, *Mar. Pollut. Bull.* 136 (2018) 61–67.
- [10] R.M. Toichuev, L.V. Zhilova, G.B. Makambaeva, T.R. Payzildaev, W. Pronk, M. Bouwknecht, R. Weber, *Environ. Sci. Pollut. Res. Int.* 25 (2018) 31836–31847.
- [11] L. Chaw Jiang, M. Basri, D. Omar, M.B. Abdul Rahman, A.B. Salleh, R.N.Z. Raja Abdul Rahman, A. Selamat, *Pestic. Biochem. Physiol.* 102 (2012) 19–29.
- [12] C.J. Lim, M. Basri, D. Omar, M.B. Abdul Rahman, A.B. Salleh, R.N.Z. Raja Abdul Rahman, *Ind. Crops Prod.* 36 (2012) 607–613.
- [13] N. Debnath, S. Das, D. Seth, R. Chandra, S.C. Bhattacharya, A. Goswami, *J. Pest Sci.* 84 (2010) 99–105.
- [14] S. Atta, M. Bera, T. Chattopadhyay, A. Paul, M. Iqbal, M.K. Maiti, N.P. Singh, *RSC Adv.* 5 (2015) 86990–86996.
- [15] G. Singh, R.S. Pai, *Expert Opin. Drug Deliv.* 11 (2014) 1023–1032.
- [16] A.B. Jindal, S.S. Bachhav, P.V. Devarajan, *Int. J. Pharm.* 521 (2017) 196–203.
- [17] C. Yang, M. Zhang, D. Merlin, *J. Mater. Chem. B* 6 (2018) 1312–1321.
- [18] Q. Gu, W. Chen, F. Duan, R. Ju, *J. Chem. Soc. Dalton Trans.* 45 (2016) 12137–12143.
- [19] N. Chaudhry, S. Dwivedi, V. Chaudhry, A. Singh, Q. Saquib, A. Azam, *J. Musarrat, Microb. Pathog.* 123 (2018) 196–200.
- [20] Z. Mohasedat, M. Dehestani-Ardakani, K. Kamali, F. Eslami, *Adv. Biores.* 9 (2018).
- [21] W. Zhang, *Proc. Int. Acad. Ecol. Environ. Sci.* 8 (2018) 1–27.
- [22] Y. Tong, L. Shao, X. Li, J. Lu, H. Sun, S. Xiang, Z. Zhang, Y. Wu, X. Wu, *J. Agric. Food Chem.* 66 (2018) 2616–2622.
- [23] A.J. Udoh, C.E. Umoh, *Indian Res. J. Ext. Edu.* 11 (2011) 6–14.
- [24] F.L. Ocho, F.M. Abdissa, G.B. Yadessa, A. Bekele, *JAIED* 110 (2016) 307–323.
- [25] M.A. Ali, I. Rehman, A. Iqbal, S. Din, A.Q. Rao, A. Latif, T.R. Samiullah, S. Azam, T. Husnain, *Int. J. Adv. Life Sci. Technol.* 1 (2014) 129–138.
- [26] M. Ragaee, A.H. Sabry, *Environ. Technol.* 3 (2014) 528–545.
- [27] M. Rai, A. Ingle, *Appl. Microbiol. Biotechnol.* 94 (2012) 287–293.
- [28] K. Qian, T. Shi, T. Tang, S. Zhang, X. Liu, Y. Cao, *Microchim. Acta* 173 (2011) 51–57.
- [29] S. Sharma, S. Singh, A.K. Ganguli, V. Shanmugam, *Carbon* 115 (2017) 781–790.
- [30] A. Bhattacharyya, P. Duraisamy, M. Govindarajan, A.A. Buhroo, R. Prasad, *Nano-biofungicides: emerging trend in insect pest control*, in: R. Prasad (Ed.), *Advances and Applications through Fungal Nanobiotechnology*, Springer International Publishing, Cham, 2016, pp. 307–319.
- [31] M.A. Alghuthaymi, H. Almoammar, M. Rai, E. Said-Galiev, K.A. Abd-Elsalam, *Biotechnol. Biotechnol. Equip.* 29 (2015) 221–236.
- [32] S.F. Adil, M.E. Assal, M. Khan, A. Al-Warthan, M.R. Siddiqui, L.M. Liz-Marzan, *Dalton Trans.* 44 (2015) 9709–9717.
- [33] S. Mishra, H.B. Singh, *Appl. Microbiol. Biotechnol.* 99 (2015) 1097–1107.
- [34] A. Dzimittrowicz, A. Motyka-Pomagruk, P. Cyganowski, W. Babinska, D. Terefinko, P. Jamroz, E. Lojkowska, P. Pohl, W. Sledz, *Nanomaterials* 8 (2018).
- [35] V. Ghormade, M.V. Deshpande, K.M. Paknikar, *Biotechnol. Adv.* 29 (2011) 792–803.
- [36] J.L. Gutiérrez, C.G. Jones, P.D. Ribeiro, S.E.G. Findlay, P.M. Groffman, *Ecosystems* 21 (2017) 1000–1012.
- [37] J.R. Hillman, C.J. Lundquist, S.F. Thrush, *Front. Mar. Sci.* 5 (2018).
- [38] M.S. Studivan, J.D. Voss, *Front. Mar. Sci.* 5 (2018).
- [39] V. Sujitha, K. Murugan, D. Dinesh, A. Pandiyan, R. Aruliah, J.S. Hwang, K. Kalimuthu, C. Panneeselvaram, A. Higuchi, A.T. Aziz, S. Kumar, A.A. Alarfaj, B. Vaseeharan, A. Canale, G. Benelli, *Aquat. Toxicol.* 188 (2017) 100–108.
- [40] H. Guan, D. Chi, J. Yu, X. Li, *Pestic. Biochem. Physiol.* 92 (2008) 83–91.
- [41] H.M. El-bendary, A.A. El-Helaly, *App. Sci. Rep.* 4 (2013) 241–246.
- [42] M.G. Paulraja, S. Ignacimuthua, M.R. Gandhi, A. Shajahan, P. Ganesan, S.M. Packiam, N.A. Al-Dhabi, *Int. J. Biol. Macromol.* 104 (2017) 1813–1819.
- [43] H. Guan, D. Chi, J. Yu, H. Li, *Crop. Prot.* 29 (2010) 942–946.
- [44] M.M. Sabbour, *Am. J. Chem.* 3 (2018) 6–10.
- [45] A. Stara, R. Belliniva, J. Velisek, A. Strouhova, A. Kouba, C. Faggio, *Sci. Total Environ.* 665 (2019) 718–723.
- [46] A. Gregorc, M. Alburaki, N. Rinderer, B. Sampson, P.R. Knight, S. Karim, J. Adamczyk, *Sci. Rep.* 8 (2018) 15003.
- [47] P.R. Whitehorn, G. Norville, A. Gilburn, D. Goulson, *PeerJ* 6 (2018) e4772.
- [48] F. Graily Moradi, M.J. Hejazi, H. Hamishehkar, A.A. Enayati, *Ecotoxicol. Environ. Saf.* 175 (2019) 155–163.
- [49] M.M. Sabbour, *Adv. Biochem. Biotechnol.* 1 (2015) 1–13.
- [50] X. Du, S.Z. Qiao, *Small* 11 (2015) 392–413.
- [51] Y. Wang, Q. Zhao, N. Han, L. Bai, J. Li, J. Liu, E. Che, L. Hu, Q. Zhang, T. Jiang, S. Wang, *Nanomedicine* 11 (2015) 313–327.
- [52] R.K. Sharma, S. Sharma, S. Dutta, R. Zboril, M.B. Gawande, *Green Chem.* 17 (2015) 3207–3230.
- [53] T.D. Pham, T.T. Bui, V.T. Nguyen, T.K.V. Bui, T.T. Tran, Q.C. Phan, T.D. Pham, T.H. Hoang, *Polymers* 10 (2018).
- [54] H. Zhou, H.-Y. Liu, H. Zhou, Y. Zhang, X. Gao, Y.-W. Mai, *Mater. Des.* 95 (2016) 212–218.
- [55] M.C. Biswas, B.J. Tiimob, W. Abdela, S. Jeelani, V.K. Rangari, *Food Packag. Shelf Life* 19 (2019) 104–113.
- [56] M. Kah, T. Hofmann, *Environ. Int.* 63 (2014) 224–235.
- [57] S. Kumar, M. Nehra, N. Dilbaghi, G. Marrazza, A.A. Hassan, K.H. Kim, *J. Control. Release* 294 (2019) 131–153.
- [58] C. Xu, L. Cao, P. Zhao, Z. Zhou, C. Cao, F. Li, Q. Huang, *Chem. Eng. J.* 348 (2018) 244–254.
- [59] M. Arias-Estévez, E. López-Periágo, E. Martínez-Carballo, J. Simal-Gaéndara, J. Mejuto, L. GarcáRío, *Agric. Ecosyst. Environ.* 123 (2008) 247–260.
- [60] M. Alexander, B. Lustigman, *J. Agric. Food Chem.* 14 (1966) 410–413.
- [61] D.A. Ellis, J.W. Martin, A.O. De Silva, S.A. Mabury, M.D. Hurley, M.P. Sulbaek Andersen, T.J. Wallington, *Environ. Sci. Technol.* 38 (2004) 3316–3321.
- [62] S.W. Baertschi, K.M. Alsante, *Stress Testing: the Chemistry of Drug Degradation*, Pharmaceutical Stress Testing, CRC Press, 2016, pp. 60–152.
- [63] M. Li, *Organic Chemistry of Drug Degradation*, Royal Society of Chemistry, 2015.
- [64] Z. Salleh, I. Wazeer, S. Mulyono, L. El-blidi, M.A. Hashim, M.K. Hadj-Kali, *J. Chem. Thermodyn.* 104 (2017) 33–44.
- [65] L. Qian, S. Wang, M. Ren, S. Wang, *Chem. Eng. J.* 366 (2019) 223–234.
- [66] M.M. Boucher, M.H. Furigay, P.K. Quach, C.S. Brindle, *Org. Process Res. Dev.* 21 (2017) 1394–1403.
- [67] F.S. Al-Mubaddel, S. Haider, W.A. Al-Masry, Y. Al-Zeghayer, M. Imran, A. Haider, Z. Ullah, *Arab. J. Chem.* 10 (2017) 376–388.



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