Volatility: a key property affecting effectiveness of arthropods' chemical defenses

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Chemical substances have a set of traits that identifies them: while chemical properties refer to changes that modify the identity of the substance, physical properties do not[1]. The latter include the boiling point (liquid/vapor state) and lipophilicity (solubility in a lipid medium[2]). Chemical defenses of insects vary in effectiveness according to the chemical group they belong to[3]. But in fact, physical properties may be even more important than considering the chemical group[4]. Our aim was to understand the role of physical properties on the effectiveness of arthropods' chemical defenses. Therefore, we considered lipophilicity (using values of log p[1] as a proxy), which may facilitate chemicals to cross cells' phospholipidic membrane and, thus, reach the site of action[5]. We also included volatility[6] (boiling point – BP – as proxy), which is related to the duration of exposure of olfactory sensilla to the chemical defense[7]. Besides physical properties, we assessed the prey model used in experiments (which we called 'prey type'); prey aggregation; quantity of chemical substances; and whether bird and arthropod predators respond differently.

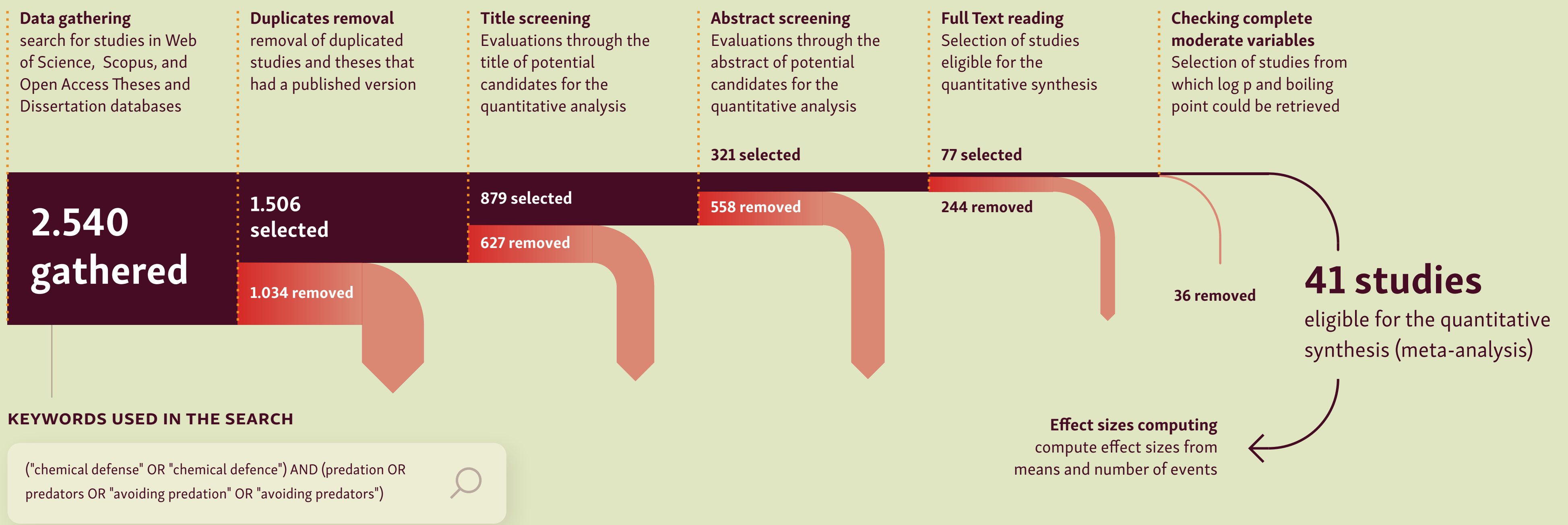
GLOSSARY

chemical group:
Atoms united in particular combinations, through covalent bonds[2] (shared electrons pairs[1]), E.g. phenol, alcohol. Different chemical substances can belong to the same chemical group

log p: *Ratio of solubility in a lipid medium to an aqueous medium[1]*

boiling point: *Tendency of a liquid change to gaseous state[6]*

To estimate the effectiveness, we computed effect sizes based on means (Standardized means difference) or number of events (Odds ratio), and converted both to Hedges'g[8]. We ran a multilevel meta-analysis, accounting for different types of dependence[9,10] and selected the best model using the Akaike Information Criterion for small samples (AICc).



Data gathering
search for studies in Web of Science, Scopus, and Open Access Theses and Dissertation databases

Duplicates removal
removal of duplicated studies and theses that had a published version

Title screening
Evaluations through the title of potential candidates for the quantitative analysis

Abstract screening
Evaluations through the abstract of potential candidates for the quantitative analysis

Full Text reading
Selection of studies eligible for the quantitative synthesis

Checking complete moderate variables
Selection of studies from which log p and boiling point could be retrieved

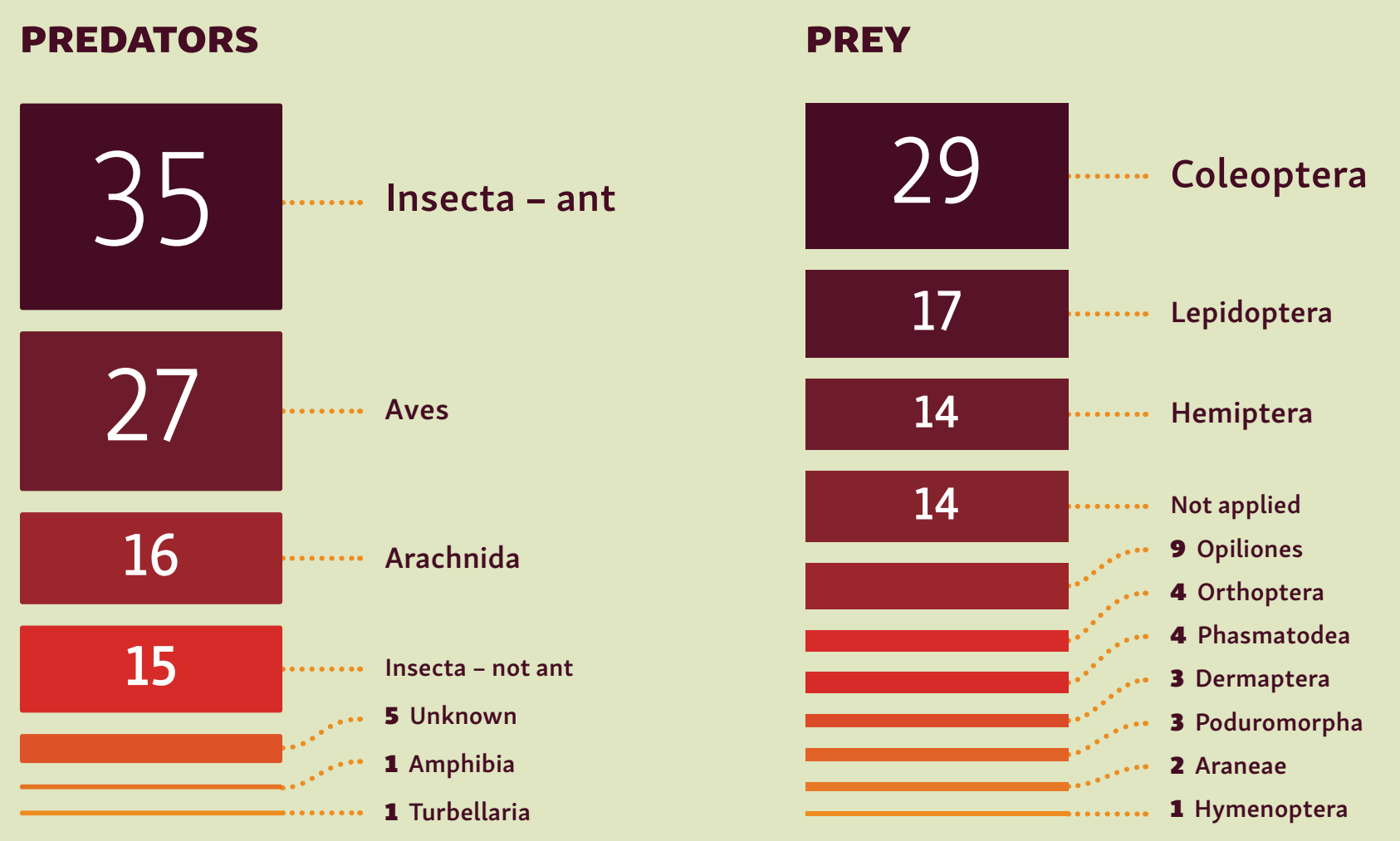
41 studies
eligible for the quantitative synthesis (meta-analysis)

Effect sizes computing
compute effect sizes from means and number of events

KEYWORDS USED IN THE SEARCH

("chemical defense" OR "chemical defence") AND (predation OR predators OR "avoiding predation" OR "avoiding predators")

Proportion (%) of predators and prey taxa from the studies included

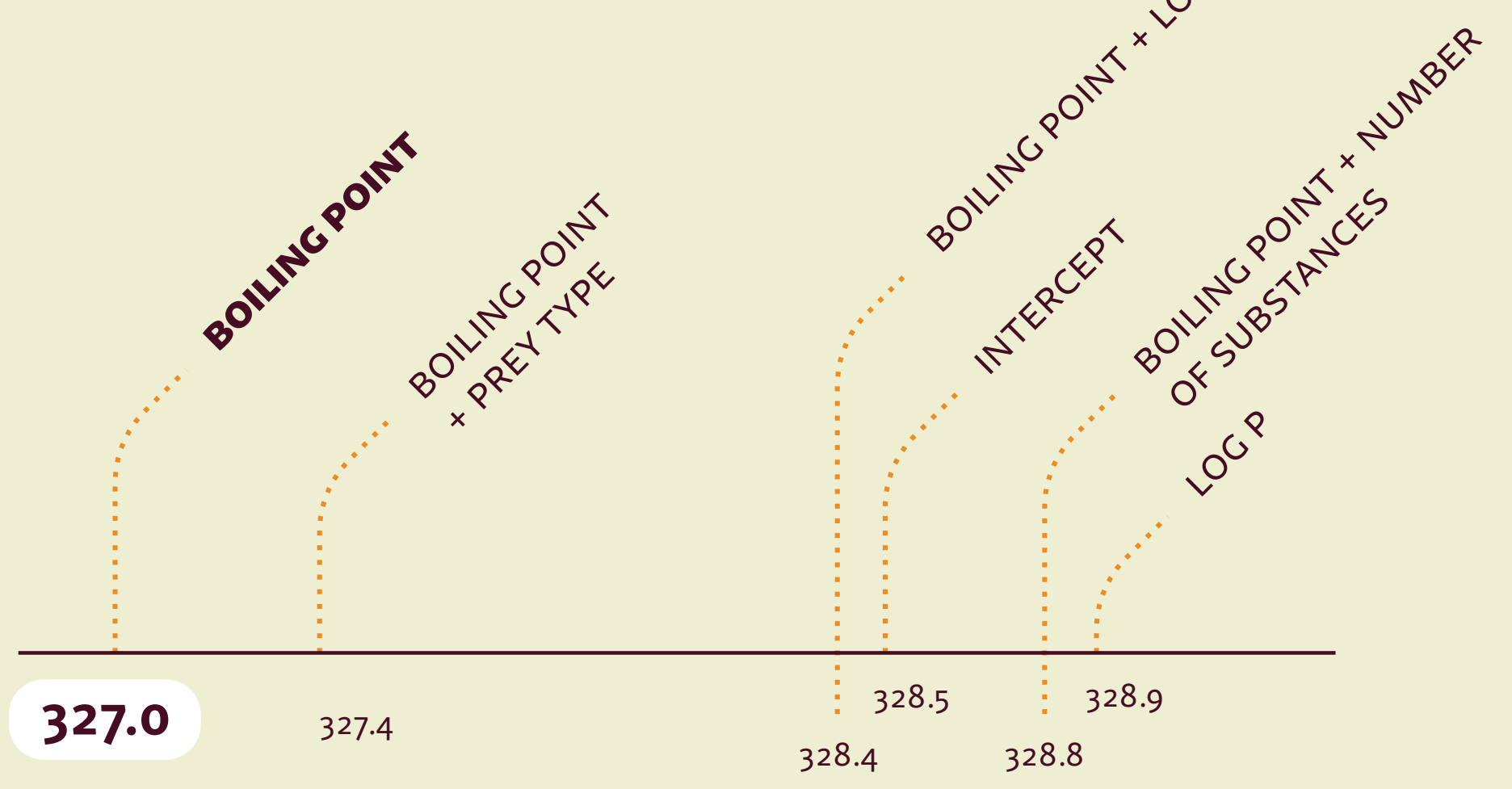


PREDATORS	
35	Insecta – ant
27	Aves
16	Arachnida
15	Insecta – not ant
5	Unknown
1	Amphibia
1	Turbellaria

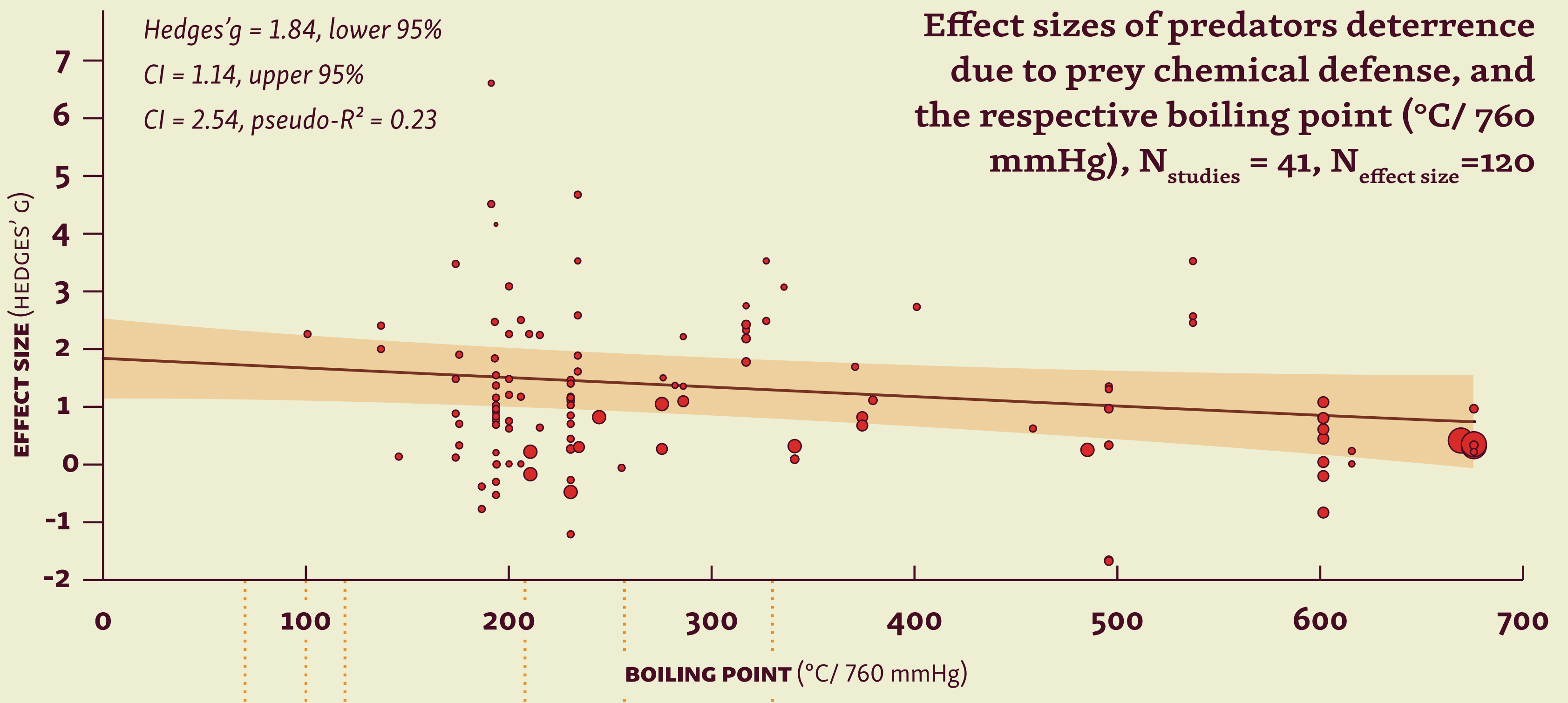
PREY	
29	Coleoptera
17	Lepidoptera
14	Hemiptera
14	Not applied
9	Opiliones
4	Orthoptera
4	Phasmatodea
3	Dermaptera
3	Poduromorpha
2	Araneae
1	Hymenoptera

The model with lowest AICc included only the boiling point, which showed a negative relationship between effect size and boiling point.

AICc values from the models with lowest AICc



Effect sizes of predators deterrence due to prey chemical defense, and the respective boiling point (°C/ 760 mmHg), $N_{studies} = 41$, $N_{effect\ size} = 120$



72.6 ± 3 ethanol

100 ± 9 water

117.1 ± 3 acetic acid

208.4 ± 9 citronellal

257.5 ± 0 diethyltoluamide

330.9 ± 15 icaridin

This means that chemical defenses in which the main substance had lower BP values, that is, higher volatility, were more effective against predation than those whose the main chemical substance had higher BPs. The values of BP of our dataset varied from 100.6 to 675.6° C/760 mmHg, with most of the frequent values around 200 - 300. Compared to common substances, such as ethanol, water, and acid acetic[11], BP values of those chemical defenses are not extremely low. Additionally, the most frequent BPs values match with values of chemical substances found in insect repellents, and insect repellency literature suggests that volatility is an essential property[12]. The effectiveness of volatile chemicals may be linked to the fact that they spread rapidly in the air, consequently: (1) it is one of the first components to be perceived by a predator, discouraging an attack[13]; (2) it is difficult to predict the localization of the emitter[14], thus it can be used in the dark[14], which might be an advantage for nocturnal animals.

In conclusion, in arthropods, the most effective chemical defenses are volatile, and this could mean that predator olfaction is a key factor for this type of defense. However, these chemical susbtances are not extremely volatile, which can suggest a trade-off between fast delivery to a predator, but not so fast that could immediately dissipate in the air.

To see the studies included in our meta-analysis scan the QR code

REFERENCES

1 Masterton WL, Hurley CN. 2015. Chemistry: principles and reactions. Cengage Learning. 7th ed

2 Abelian A, Dybek M, vvWallach J, Gaye B, Adejare A. 2021. Pharmaceutical chemistry. In: Adejare A. Remington: The Science and Practice of Pharmay. 23rd ed. 103–128

3 Zvereva EL, Kozlov MV. 2016. The costs and effectiveness of chemical defenses in herbivorous insects: A meta-analysis. Ecol Monogr. 86(1):107–124

4 Tschinkel WR. 1975. A comparative study of the chemical defensive system of tenebrionid beetles: Chemistry of the secretions. J Insect Physiol. 21(4):753–783

5 Cronin MD. 2006. The Role of Hydrophobicity in Toxicity Prediction. Curr Comput Aided-Drug Des. 2(4):405–413

6 Speight JG. 2017. Properties of Organic Compounds. In: Environmental Organic Chemistry for Engineers. Butterworth-Heinemann. 1st ed. 87-151

7 Nerio LS, Olivero-Verbel J, Stashenko E. 2010. Repellent activity of essential oils: A review. Bioresour Technol. 101(1):372–378

8 Borenstein M, Hedges LV, Higgins JPT, Rothstein HR. 2009. Introduction to Meta-Analysis. John Wiley & Sons, Ltd. 1st ed

9 Lajeunesse MJ. 2009. Meta-Analysis and the Comparative Phylogenetic Method. 174(3): 369-381

10 Nakagawa S, Santos ESA. 2012. Methodological issues and advances in biological meta-analysis. Evol Ecol. 26(5):1253–1274.

11 ChemSpider | Search and share chemistry. [accessed 2021 Jun 21]. https://www.chemspider.com/.

12 Moore SJ, Debboun M. 2006. History of insect repellents. In: Insect Repellents: Principles, Methods, and Uses. Debboun M, Fraces S, Strickman D, editors. Taylor & Francis. 1st ed

13 Eisner T, Grant R. 1981. Toxicity, odor aversion, and "olfactory aposematism". Science. 213(4506):476–476.

14 Wyatt TD. 2003. Animals in a Chemical World. In: Pheromones and Animal Behaviour: Communication by Smell and Taste. Cambridge University Press. 1st ed. 1-22

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