Emerging Pollutants of Environmental Concern

Volume 1: Neonicotinoids

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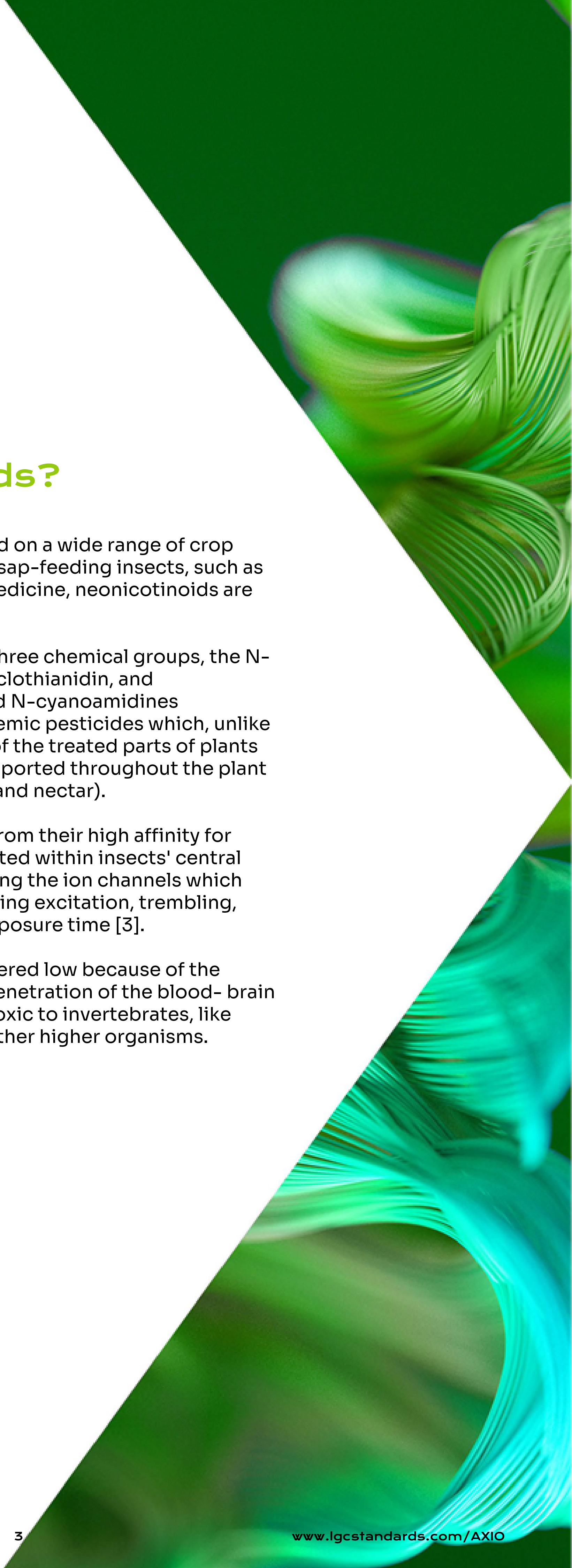
What are Emerging Pollutants?

The attention of analytical laboratories and legislators is moving from the 'traditional' pollutants to a new group of 'emerging' environmental contaminants. These emerging pollutants are increasingly of concern due to their widespread occurrence, their potential toxicity to mammals or other biotas, and their ability to persist in the environment, often resulting in bioaccumulation.

Pollutants are typically introduced into the environment as a result of human interactions and processes, and include perfluorinated compounds, nanomaterials, pharmaceuticals, illicit drugs, antibiotics, hormones, flame retardants, disinfection by-products (DBPs), artificial sweeteners, pesticides, benzotriazoles, 1,4-dioxane and algal toxins. Some of these compounds have the potential to pose a threat to the environment and affect the stability of global ecosystems which we all depend upon. There are significant differences in chemicals registered for use and mixtures of chemicals across different parts of the world – with complexity increased by the high volume: over 350,000 worldwide. [1] The chemicals bring many benefits to society, but overuse is causing harm to the environment and consequently to our health.

Testing for this wide range of compounds may require novel analytical techniques and/or monitoring strategies to determine concentrations in the µg/L concentration range or lower. In order to accurately determine the environmental fate of the emerging pollutants, the sampling and analysis of water, soil, sediments, and biota must be carried out.

In the first of a series of white papers exploring emerging pollutants of environmental concern, we will be looking at the implications of neonicotinoids. AXIO Proficiency Testing will be drawing on over 40 years of experience in environmental quality assessment, to explore historic and current legislative and regulatory requirements, as well as the challenges facing laboratories responsible for the accurate monitoring and measurement of neonicotinoids.



What are Neonicotinoids?

Neonicotinoids are a group of insecticides used on a wide range of crop types, to control a variety of pests, particularly sap-feeding insects, such as aphids and root-feeding grubs. In veterinary medicine, neonicotinoids are used for tick control and in flea collars for pets.

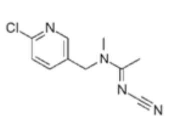
Neonicontinoids can be classified into one of three chemical groups, the N-nitroguanidines (imidacloprid, thiamethoxam, clothianidin, and dinotefuran), nitromethylenes (nitenpyram) and N-cyanoamidines (acetamiprid and thiacloprid). [2] They are systemic pesticides which, unlike contact pesticides that remain on the surface of the treated parts of plants (e.g. leaves), are taken up by the plant and transported throughout the plant (leaves, flowers, roots, stems, as well as pollen and nectar).

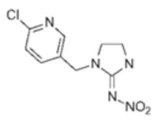
The mode of action of neonicotinoids derives from their high affinity for nicotine acetylcholine receptors (nAchRs) located within insects' central nervous system. Neonicotinoids work by opening the ion channels which allow the entry of Na + and Ca 2+ into cells causing excitation, trembling, paralysis, and death depending on dose and exposure time [3].

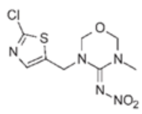
In vertebrates, neonicotinoid toxicity is considered low because of the relatively low affinity of the nAchRs and poor penetration of the blood- brain barrier, hence neonicotinoids are much more toxic to invertebrates, like insects, than they are to mammals, birds, and other higher organisms.

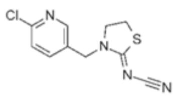
History & Legislation

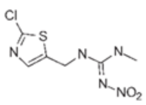
Neonicotinoids were developed in the 1980s, and the first commercially available compound, imidacloprid, has been in use since the early 1990s [4]. The first neonicotinoid was approved for use as a plant protection product in the EU in 2005. Additional neonicotinoid insecticides were subsequently approved as active substances in the EU for the use in plant protection products, namely clothianidin, imidacloprid, thiamethoxam, acetamiprid and thiacloprid.


Acetamiprid


Imidacloprid


Thiamethoxam


Thiacloprid


Clothianidin

As a result of numerous scientific studies on the link between neonicotinoid usage and honey bee mortality [5], legislation of neonicotinoids has focussed on restricting their use in order to protect non-target insects, particularly honey bees. In 2013, the European Commission severely restricted the use of plant protection products and treated seeds containing three of these neonicotinoids (clothianidin, imidacloprid and thiamethoxam) to protect honey bees (Regulation (EU) No 485/2013). This legislation prohibited the use of the three neonicotinoids in bee-attractive crops and required the applicants for the three substances to provide further data to confirm the safety of the uses still allowed. Following the assessment of this confirmatory information by the European Food Standards Agency (EFSA) the remaining outdoor uses could no longer be considered safe due to the identified risks to bees. Therefore, in 2017 the Commission services prepared three proposals to completely ban the outdoor uses of the three active substances.

Other EU decisions and subsequent regulations have been introduced for other neonicotinoids; acetamiprid was identified by EFSA as a low risk to bees and a ban or further restrictions of this substance were therefore considered to be neither scientifically nor legally appropriate. In contrast the approval of a fifth neonicotinoid, thiacloprid was withdrawn on 3 February 2020 after a peer review of the risk assessment which had been carried out.

In the United States, the Environmental Protection Agency has proposed interim decisions for five neonicotinoid chemicals which aim to:

- Keep pesticides on the intended target
- Require additional personal protective equipment
- Place restrictions on when pesticides can be applied to blooming crops
- Advise homeowners against the use of neonicotinoid products
- Cancel the use of imidacloprid on residential turf

Environmental Fate

Neonicotinoids are water-soluble and break down slowly in the environment, properties which are key to their systemic mode of action as this enables them to be taken up by the plant and provide protection from insects as the plant grows. The degree of water solubility depends on the compounds themselves, the form of the application and the local conditions, such as ambient temperature and water pH.

Water solubility means that any of the chemical which is not taken up by the plant may be a risk to the aquatic environment. The primary mechanism for transport of neonicotinoids into water bodies appears to be via rainfall run-off during or shortly after the planting season, though minor modes have been identified via direct contact with treated seeds, spray drift, leaching into groundwater and the decay of treated plant material [6].

Exposure of neonicotinoids to sunlight results in relatively rapid photodegradation; under natural light in rice paddies in Japan, imidacloprid was shown to have a half-life of 24.2 hours [7]. Under laboratory conditions researchers measured half-lives for five neonicotinoids under differing conditions to mimic the seasonal change found in Canada. They found 7-8- fold variations in the rate of neonicotinoid photolysis due to the variation in light levels across the season, results which are broadly similar to previously published studies with nitro-substituted neonicotinoid half-lives in the region of <1 – 3 days depending on light levels [8].

Neonicotinoids have been shown to have considerable persistence in soil; a review of available half-lives from field and laboratory studies conducted between 1999 and 2013 showed that reported half-lives are highly variable and typically range from 200 days to in excess of 1000 days for imidacloprid, 7–353 days for thiamethoxam and 148-6931 days for clothianidin. The half-lives of the nitro-substituted neonicotinoids appear to be shorter, at 3-74 days for thiacloprid and 31-450 days for acetamiprid. Half-lives of over 1 year would suggest the likelihood of neonicotinoid accumulation in the soil, assuming continuous input [5]. This potential for accumulation in the soil suggests the formation of a 'bank of stored neonicotinoids' and a constant source of exposure for soil dwelling organisms.

Monitoring Strategy & Measurement of Neonicotinoids

Five neonicotinoids (Imidacloprid, Clothianidin, Thiamethoxam, Acetamiprid and Thiacloprid) were included in the EU 'Watch List' of 17 chemicals in March 2015, which required each member state to monitor at least annually for a minimum number of monitoring sites.

The UK monitoring of the EU Watch List was first carried out in 2016 for these five compounds, across 23 sites (16 in England, four in Scotland, and three in Wales), 17 were found to be contaminated with neonicotinoids, with 88% of samples taken found to contain one or more of the compounds of interest. The average detected neonicotinoid concentrations ranged from 0.002 to 0.443 µg/l. Eight of the monitored rivers in England exceeded recommended chronic pollution limits, and two were classified as acutely polluted. Surprisingly, Imidacloprid was detected in a number of arable river catchments despite it having very little use on arable fields in 2016 or the preceding few years [9].

Numerous authors in multiple countries have reported studies of neonicotinoid monitoring in surface waters over a number of years. A review of the literature for 29 studies, from nine countries found that neonicotinoids were detected in the majority of the water samples, irrespective of the water type; puddled water, irrigation channels, streams, rivers or wetlands [10]. The concentration data indicated an average surface water concentration of 0.13µg/L and a peak concentration, when the concentration increases dramatically during or shortly after the planting season, of 0.63µg/L.

"A review of the literature for 29 studies, from nine countries found that neonicotinoids were detected in the majority of the waters sample, irrespective of the water type"

Analytical Methodology & Techniques

Neonicotinoids, in common with many other insecticides, are detected by traditional methods such as gas chromatography coupled with different detectors and liquid chromatography-mass spectrometry (LC-MS, LC-MS/MS), which have been shown to have low detection limits and acceptable sensitivity and selectivity [4].

In the quantitative analysis of neonicotinoids, sample preparation is typically carried out in order to remove interfering species and increase the concentration of the analyte(s) in the test sample. Almost all of the common sample preparation methods (liquid-liquid extraction, solid phase micro-extraction, dispersive solid phase extraction) have been applied to the determination of neonicotinoids however the use of solid phase extraction (SPE) is one which has been extremely widely reported.

After extraction, gas chromatography (GC) and liquid chromatography (LC) techniques are applied for the simultaneous measurement of the neonicotinoids and their important metabolites. Many of the analytical methods reported employ mass spectrometry detection, as this can offer better sensitivity for the compounds of interest. Where a simple matrix is being analysed, the use of LC-MS/MS for the final measurement, has enabled the simultaneous analysis of multiple neonicotinoids without any sample preparation [11].

Detection limits using GC and LC methods, have been reported within the range from 0.1 to 1 ng/l, although the limits of detection for some of the metabolites may be slightly higher [4].

AXIO Proficiency Testing Insights into Testing Methods

Although the concentrations of the Neonicotinoids in environmental materials are low, typically around 1-10 ng/L, in the AXIO Proficiency Testing AQUACHECK scheme, samples are provided at similar concentrations for the analysis of a range of pesticide residues, such as phenoxy herbicides, triazine herbicides, phenylurea herbicides, insecticides and fungicides.

The results returned by participants for these samples typically results in a high proportion of satisfactory performance scores.

The increasing use of direct injection methods for the analysis of pesticides at concentrations of environmental concern has typically resulted in a smaller spread of data, as measured by the robust standard deviation, due to the removal of sample preparation steps and a consequential reduction in the measurement uncertainty. This improvement in method performance as participants adopt this technology, has resulted in a subsequent increase in the proportion of results which receive a satisfactory performance score.

Conclusion

Neonicotinoids have been used as agricultural pest control products and veterinary medicines in more than 120 countries around the world, making them the most widely used class of insecticides. This prevalence in the environment combined with their stability over time and their ability to infiltrate aquatic systems has led to increasing regulation in many areas of the world, driven both by environmental studies and ever-increasing public awareness of the subject.

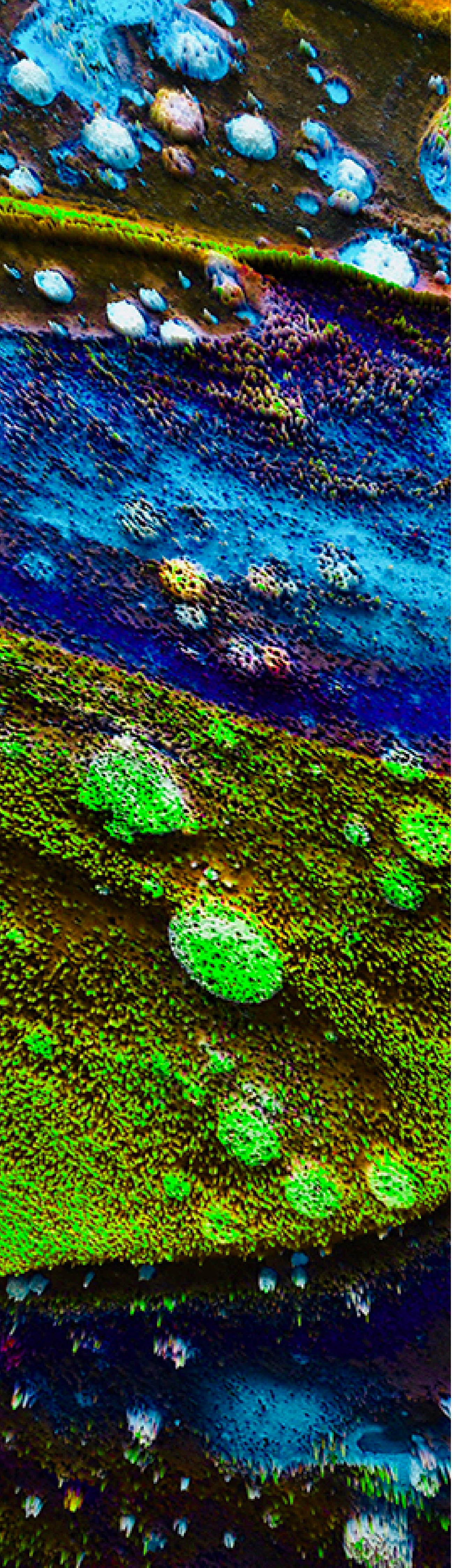
This regulation is supported by an increase in the monitoring of neonicotinoids in soils and in aquatic systems, meaning laboratories all around the world need to maintain pace with the evolving neonicotinoid and wider insecticides testing environment. As always, it is essential that this analysis delivers reliable and trustworthy measurements to support meaningful outcomes.

In order to ensure that testing is being carried out correctly and consistently at the concentration levels required for analysis of neonicotinoids in aquatic systems, a robust quality system is required, and should include regular participation in a proficiency testing (PT) scheme as well as appropriate use of relevant reference materials.

AXIO has expanded its AQUACHECK scheme to include a new PT sample, PT-AQ-66 for the quantitative determination of neonicotinoids includes the five most agriculturally and environmentally important compounds, acetamiprid, clothianidin, imidacloprid, thiacloprid and thiamethoxam, at concentrations in the environmentally relevant level of 0.01 to 0.15µg/l

About AQUACHECK

AXIO Proficiency Testing offers the industry- leading AQUACHECK scheme that has been in continuous operation since 1985. Test materials are provided for the analysis of major inorganic/ organics, metals, phenols, organochlorine pesticides, and many others. Participation in the AXIO AQUACHECK scheme allows laboratories to identify problems before they affect the quality and safety of waters. Participants will be able to demonstrate independently that they are producing accurate and meaningful results to laboratory management and customers.



About the Author

Dr. Matthew Whetton

Dr Matthew Whetton is the Head of Technical Operations for the Proficiency Testing group at LGC Standards and has almost 15 year's experience in the field.

In this role Matthew is responsible for the production, development and technical operation of over fifty proficiency testing schemes, covering Chemistry, Clinical analysis and microbiological testing in a diverse range of analytical fields, and now incorporating neonicotinoids and wider insecticide groups

Prior to joining LGC, Matthew has previously carried out a variety of roles in the fields of phytochemistry and analytical services, spending more than 10 years working in the field of analytical chemistry and specialising in the analysis of pesticides in food and environmental matrices.

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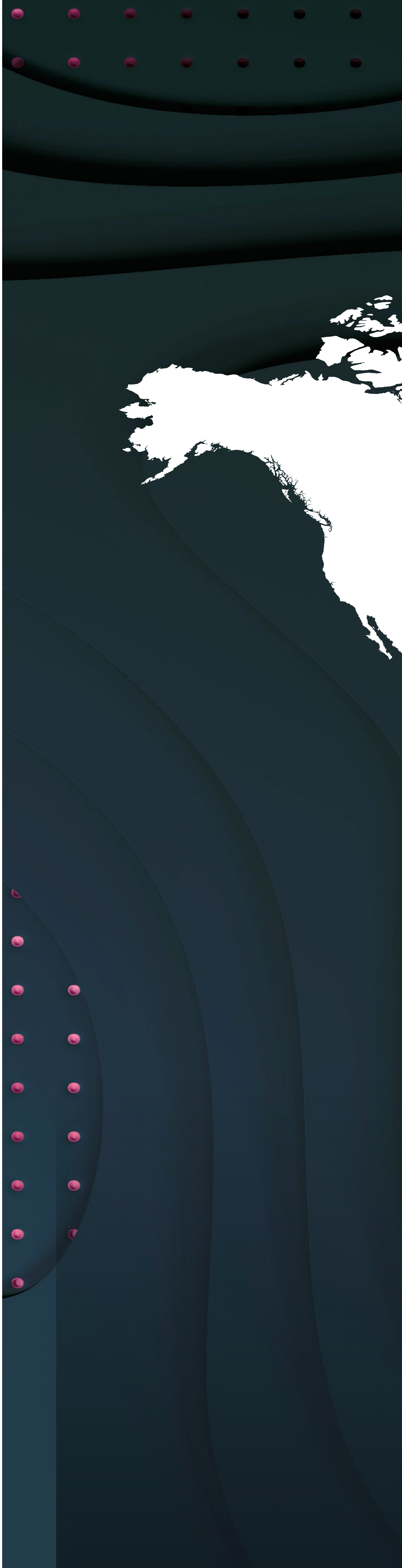

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