Reception: **December 7, 2021** | Acceptance: **June 9, 2022** | Publication: **October 1, 2022**

A review on birds of prey migration and the toxicological effects of heavy metals

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To quote this article:

Becerril González, M. (2022). Una revisión sobre la migración de las aves rapaces y los efectos toxicológicos de los metales pesados. *Espacio I+D, Innovación más Desarrollo, 11*(31). https://doi.org/10.31644/IMASD.31.2022.a03

— Abstract—

In this work, the importance of migrating birds of prey as bioindicators to show the presence and concentration of heavy metals and metalloids is examined, adittionally, a general view of the toxicity of these elements is discussed. Human activities such as mining, the petroleum/oil industry, and agriculture are the principal sources of environmental pollution, the effects of these industries on the health of migrating raptors are variable, at present, studies to determine the degree to which raptors are affected are being conducted. Some heavy metals and metalloids have negative effects on biomolecules essential to cell metabolism; despite the number of written works on the subject, their results are inconclusive, and changes in natural populations of raptors are diverse.

Keywords:

Birds of prey; migration; indicator species; heavy metals; Veracruz Rio de Rapaces.

CURRENT TALKS ON THE SUBJECT

Various environmental issues have caught our attention in the last six decades, particularly those studies that account for the negative effects we have caused as a society on ecosystems, these are diverse and have caused effects of different magnitudes, however, increasing scientific evidence and new knowledge are provided to assemble the intricate environmental puzzle, with its key pieces and processes that keep it in balance.

It is worth mentioning that one of the ways we can know the impacts of environmental pollution is the presence or absence of what we know today as bio-indicator species,[1] several of them we can "evaluate" due to specific study techniques that lead us to know aspects of particular interest, for example, the toxicity that can generate an element or chemical compound, adversely affecting some metabolic function of a living being.

Activities such as mining, petrochemicals, agriculture, and industry in general, are responsible for the generation of a series of highly polluting waste or use in their processes the so-called heavy metals and metalloids (*e.g.*, cadmium, chromium, mercury, lead, zinc, arsenic, among others), these can provide us with information not only on the levels of environmental pollution, but, in addition, they allow us to evaluate the health status of indicator species, such is the case of birds of prey (Figure 1), this group of birds is classified into diurnal raptors such as eagles, hawks, sparrowhawk, kestrels, etc., and nocturnal raptors such as owls and tecolotes[2] the majority are, unfortunately, under some category as endangered species or with populations very vulnerable to decline.

Figure 1. Photograph of *Rupornis magnirostris*, juvenile individual, Roadside hawk, Papantla, Veracruz, bird of prey resident in Mexico and with wide distribution in South America. Source: Own elaboration (2018)

1 They are the species that provide us with very valuable information, and which can be analyzed qualitatively and quantitatively to know the state of conservation or alteration of ecosystems.

2 Birds of prey or raptors are made up of four Orders: Strigiformes (owls and related), Cathartiformes (New World vultures), Accipitriformes (eagles and related), and Falconiformes (hawks and related) and seven families with more than 500 species on all continents (Del Hoyo & Collar, 2014).

It is pertinent to mention that because birds of pray are part of charismatic birds, they have been studied from different points of view, among which are the study of their conservation, geographical distribution, migration, spatial modeling, the assessment of landscape conditions, and the use of geographic information systems (Rodríguez-Estrella & Bojórquez, 2004).

BIRDS OF PREY MIGRATION IN THE WORLD

The migration of birds is one of the natural phenomena of greatest interest in ornithology (i.e., the study of birds), although many things are known in this regard, there are still unknown basic and specific aspects of this extraordinary journey; at least in birds there is a record of 1,855 species that migrate annually (BirdLife, 2004a, and 2004b), these migrations can be a long or short distance, from north to south or from east to west, it is presented cyclically, and it has been said that it is the result of avoiding low temperatures, having access to food or having suitable sites for reproduction, whatever the case may be, during the movement through the various migratory routes the birds can be analyzed and thus determine their health status. There are two major birds of prey migratory routes recognized globally, one follows the migration from northeast Africa to Asia and ends in the central and northern part of Europe, this has been studied by the German Ornithologists' Society (Bairlein, 2003) and BirdLife International, and the other in the north-central-south of the American continent, analyzed by Cornell University of New York, through the Cornell Lab, the Audubon Society and in Mexico by the Asociación Civil Pronatura Veracruz since 1991.

Mexico is one of the countries that offer a unique opportunity for the observation and registration of migratory species. Some reports mention that just over 300 species can be recorded weekly, well above other tropical and subtropical sites in the world, for example, in the state of Veracruz alone there are more than 50 important sites for observation with the presence of more than 700 autumn migratory species in total (Straub, 2007). Some data shared by the National Commission for the Knowledge and Use of Biodiversity mention that in the migration of "Veracruz Río de Rapaces" only in 2005 there were 5,691,204 individuals belonging to 25 birds of prey species and four unidentified genera, which reveals the magnitude of migration in the Gulf Coastal Plain.

Migratory birds of prey present serious problems due to the change in land use for agriculture-related purposes, since it involves 80% of migratory birds of prey (Kirby *et al.*, 2008), in addition to the use of organochlorine pesticides and fertilizers, it should be noted that many of the companies dedicated to the synthesis of these products present partial information and in few cases the risks to health and ecosystems are mentioned in general, some of them apparently are not even regulated by environmental laws, just remember the use of FURADAN 350 L (*i.e.*, Carbofuran: 2-3-dihydro-2,2-dimethyl-7-benzofuranyl-methyl carbamate) to fight the nematodes "roundworms" in Africa that has caused the death of lions and as of yet, an undetermined number of vultures of various species, thus breaking the ecological balance, this product in Mexico is used in various crops (*e.g.*, peanut, coffee, sugar cane, chili, pumpkin, melon, cucumber, watermelon, strawberry, corn, potato, banana and wheat among others) especially for its availability and low price ($978.00 pesos per liter/quoted as of November 2021 in Mercado Libre) and its specific effects on wildlife are still unknown.

Undoubtedly, the health assessment of migratory raptors is of vital importance, due to the eco-physiological conditions necessary to carry out the complete migration since they face the destruction of their habitat and climate change, and if it were not enough, the same health conditions of the bird (Klaassen *et al*., 2012), in these cases the energy needs of ATP (adenosine triphosphate, a highly energetic molecule used in cell metabolism) by aerobic and anaerobic routes are related to efficient metabolic processes and, in turn, with the health status of individuals, whether young or adult. On the other hand, a clear relationship has been observed between the absence of migratory species and the loss of ecological and evolutionary relationships.

BIRDS AS BIO-INDICATORS OF HEAVY METALS

In the specific case of birds of prey, as they are species positioned at the top of the food chain, they can be used as bio-indicator species (Figure 2), and therefore, their monitoring is a matter of high priority for experts since they are individuals who help determine the presence of heavy metals and their effect on other fauna and flora in general (Hermoso de Mendoza *et al*., 2006).

Regarding the biology of birds of prey, it should be noted that they are part of the birds' wildlife that presents long life cycles, some travel long distances, and others are part of the "sanitary body" of nature (*i.e.*, scavengers) that are responsible for cleaning the ecosystem of dead animal bodies or trap sick animals, that does not mean that they do not feed on healthy animals (*i.e.*, hunters), but we can imagine the intricacy of the problem to be studied, some of these birds of prey feed on other birds, mammals of various sizes, reptiles, amphibians, fish and even some include insects and mollusks in their diets. This can also help to understand the different concentrations of heavy metals present and even depend on the region where the bird is distributed and the season of the year, as well as the age of the individuals and their sex.

Figure 2. Photograph of *Accipiter cooperii*, adult individual, Cooper's hawk, Mayor's Office Miguel Hidalgo, Second Section of the Chapultepec Forest in Mexico City, bio-indicative and migratory bird of prey in "Veracruz Río de Rapaces". Source: Own elaboration (2018)

The most complete studies have been carried out in the Gulf Coastal Plain since they are very close to reality; their methodology includes working with all the migratory raptors trapped throughout each year, this has been done in little more than 20 years, taking samples of blood and feathers from live birds of prey for subsequent release; these studies have been analyzed by high-level task forces, as directed in the state of Veracruz by Dr. Ernesto Ruelas Inzunza of the Universidad Veracruzana y Pronatura Veracruz, obtaining valuable information on this subject.

As a general evaluation of heavy metals and metalloids in living beings, various effects are presented at the molecular level, within which we can observe the following:

1. Blockade of functional groups in biomolecules, due to the affinity of metal cations for the sulfhydryl groups of proteins, specifically cysteine residues, which causes their denaturation (Schützendübel & Polle, 2002; Peralta-Videa *et al.*, 2009).
2. Displacement of cationic sites in important enzymes, so they lose their function (Schützendübel & Polle, 2002; Smeets *et al.*, 2005).
3. Formation of reactive oxygen species due to the autooxidation of metals such as Fe^{2+} (iron ion) or Cu^{+} (copper ion), resulting in the formation of H_2O_2 (hydrogen peroxide) and the OH radical (hydroxyl), in the first case, it has been observed that its accumulation considerably increases programmed cell death (*i.e.*, apoptosis), while the OH radical is one of the most reactive known for its ability to initiate free radical chain reactions that cause modifications and irreversible

damage to cellular molecules such as carbohydrates, DNA (deoxyribonucleic acid), proteins and lipids (Mithöfer *et al.*, 2004).

BAD MEMORIES OF PAST EXPERIENCES

For just over 50 years, there had been deaths of adult individuals and chicks of White-headed Eagles (*Haliaeetus leucocephalus*) due to lead poisoning; in those cases, the concentrations ranged from 5-61 ppm (parts per million) and 5-12 ppm respectively. This caught the scientific community's attention dedicated to dealing with environmental pollution issues by chemical substances. The most immediate thing was to detect the sources to prolonged exposure in these raptors, even when it was referred to that this only happened in underdeveloped countries in tropical and subtropical areas. Currently, the evidence suggests the opposite and establishes, unfortunately, a generality in terms of prolonged exposures and absorption of heavy metals in many developed or non-developed countries, whose environmental policies have been insufficient to curb these problems. The truth remains that birds have high and lethal concentrations of one or more of these chemical elements.

Mining in our country is one of the leading causes of environmental pollution by heavy metals due to the inadequate management of its waste known as "mining tailings" reports indicate that in Mexico, there could be millions of tons of tailings scattered in the national territory, of which its conditions and its potential to affect the environment are still unknown (Yañez *et al.*, 2003; Meza-Figueroa *et al.*, 2009; Mireles *et al.*, 2012; Cortés-Jiménez *et al.*, 2013; Ramos-Arroyo & Siebe-Grabach, 2006)

HEAVY METALS AND METALLOIDS PRESENT IN BIRDS OF PREY, RECENT STORIES WITH SCIENTIFIC EVIDENCE

For some time, the effect caused by various concentrations of heavy metals and metalloids in the liver tissue of birds of prey has been investigated, as in some areas of Spain, where "normal concentrations of As (arsenic), Cd (cadmium), Pb (lead) and Zn (zinc)" apparently have no toxicological severe effects on their health (Hermoso de Mendoza *et al.*, 2006), however, these data are not entirely conclusive, it is worth mentioning that information from various sources should be checked and strict methodologies used to assess the impact on the environment. In the previous study, for example, nine birds of prey species were analyzed for a total of 85 individuals, of which three species were analyzed, three individuals of each, and of one species, 44 specimens were studied; the latter represents 51.7% of the samples analyzed, suffice to mention that only in Spain have been recorded 33 species of birds of prey.

In several wild species, including the White-headed Eagle and the Golden Eagle (*Haliaeetus leucocephalus* and *Aquila chrysaetos* respectively), blood tests have reported harmful effects on the neurological system, as well as on the reproductive system, resulting from high concentrations of arsenic, and mercury and lead (Lehner *et al.*, 2013).

In species such as the Californian Condor (*Gymnogyps californianus*), which is endangered (SEMARNAT, 2010. NOM-059-SEMARNAT-2010) and whose eating habits place them within scavenger raptors, lead exposure is very high when lead munitions residues have been found in dead animals, causing harmful effects on synaptic activity and problems in bone tissue conformation (Hunt, 2012), in addition to shortening longevity and having negative effects on reproduction (*e.g.*spermatogenesis). In the same case of ingestion by meat contaminated by Pb are Golden Eagles (Iwata *et al.*, 2000; Hunt *et al.*, 2006; Krone *et al.*, 2009), Old World Vulture and Hawks of various species (Mateo, 2009; Fisher *et al.*,2006).

In the American Kestrel (*Falco sparverius*), δ-aminolevulinic acid is a precursor in the synthesis of hemoglobin, however, its concentration can be elevated due to lead poisoning, affecting, in turn, the synthesis of porphyrins that result in hemoglobin part of the heme group not being produced properly, and therefore, the transport of oxygen to the body is not carried out properly (Pattee, 1985).

Nighat and his colleagues studied five species of the Family *Falconidae* (*falcons*), nine of *Accipitridae* (*eaglets*), and four *Strigidae* (*owls*) in Pakistan in 2013 due to the current high concentrations of heavy metals in the country to implement remedial measures. Although, the results have been mixed in terms of concentrations, in all cases they have been detected and show a devastating ecological crisis due to industrialization; particularly in South Asian countries, exhibiting, inter alia, inadequate solid and liquid waste management in urban areas (Karn & Harada, 2001; Hinrichsen *et al.*, 1997; Pandey, 2006).

Arsenic

Birds of prey allow us to evaluate specific cases such as arsenic, where said element, in addition to being carcinogenic, is a bioaccumulative toxic (Hermoso de Mendoza *et al.*, 2006). Currently, research is being carried out to study the food contents of various species of birds, especially raptors, because traces have been found in some stomach remains. Possibly, its use as FeAsS arsenopyrite in agricultural products as pesticides and herbicides (Londoño-Franco *et al.*2016) is one of the main routes of direct ingestion. The feeding habits of some raptors include small and medium-sized mammals found in farmland that eat heavy metals in their usual diet.

Cadmium

The case of cadmium is different since it shows recent exposure to some blood source and prolonged exposure in feathers, however, variables such as age, the time of sampling, the site where it was taken should be considered, etc. However, it is seen that juvenile individuals present lower concentrations, and adult birds of prey multiply up to ten times their concentration (Hermoso de Mendoza *et al*., 2006). The effects (as well as the presence of lead) on the endocrine system of birds can affect development and growth, feather molting, and migration (Stoica *et al*., 2000; Martin *et al*., 2003), cause respiratory diseases and inhibits egg production and shell thickness.

Cd when used as part of some fertilizers can be present in soil and water bodies due to some medications (Figure 3), we can also find it in cereals, vegetables, and tubers (Londoño-Franco *et al*., 2016) that are part of the diet of some rodents and therefore can be the route of direct ingestion by birds of prey.

Figure 3. Photograph of *Pandion haliaetus*, adult individual, Osprey, Tecolutla, Veracruz, some individuals have lethal concentrations of Cd due to their strictly piscivorous diet. Source: Own elaboration (2020)

Chromium

The presence of Cr has shown that it is an element that causes damage to genetic material (*i.e*., mutagenic agent), and in general, to eukaryotic cells of many species (Robles-Camacho & Armienta, 2000), obviously high non-lethal concentrations of chromium have been found in birds of prey, research continues as it is an essential micro-mineral in lipid metabolism, carbohydrates and proteins, however, the various results raise more specific studies in this regard.

Mercury

Blood, feather, and egg tests for White-headed Eagle (*Haliaeetus leucocephalus*) chickens, at some U.S. sites, reveal that in 95% of the samples Hg is found and that in most of the concentrations are low (0.025-0.079 mg/kg – ppm), the presence of mercury is correlated with the diet of the species. However, it is important to remember that some studies establish that in adult individuals the number of heavy metals can be ten times higher than in juvenile individuals or chickens. Interestingly, some evaluations consider that for this species between 2008 and 2010 the amount and concentration of mercury in blood and feathers has been decreasing (Mojica & Watts, 2011).

For their part, Carlson and collaborators, in 2012, found mercury in all blood samples analyzed in the same species, on average 0.28 ppm, and in chickens, it was observed that in 7.8% of cases, had high levels, greater than 0.7 ppm, this can generate in various toxicological effects in the medium and long term during the individuals' development.

In the Red-breasted Eagle (*Buteo lineatus*) the levels detected of Hg are alarmingly high in blood and feathers, both in chickens and adult individuals (Hanneman, 2021), so we should not think about generalizing these situations at any time, in some species the risks of toxicity are greater for others, as a result of their eating habits, geographical distribution or exposure times to various chemical elements, among other variables.

In our country, Campbell (2018), has found a higher concentration of mercury in blood samples in resident birds of prey such as the Short-tailed Eagle, Striped Falcon and Road Eagle (*Buteo brachyurus, Falco femoralis* and *Rupornis magnirostris*, respectively) while in migratory raptors such as Cooper's Hawk and Cinnamon-breasted Hawk (*Accipiter cooperii* and *Accipiter striatus*) the highest concentration of the same element is greater in feathers, which clearly suggests that raptors in general present contamination in their body by the presence of Hg and are exposed and ingest this heavy metal. Whatever the case, we can clearly associate it with the reproduction-nesting sites in the north of the American continent and their resting sites along the migratory routes where industrial activities and urban areas generate pollution due to the large amount of these metals, in the Mexican case it is possible that having carried out this work in the state of Veracruz, which is characterized by its petrochemical activities, the concentrations are expected to be high due to the food and its position in the food chain.

In many countries, mercury can be detected in water, such samples have been taken from natural sources such as rivers, wetlands, lakes, coastal areas, and oceans where birds of prey consume fish contaminated with various heavy metals, including mercury. In industrialized countries, water pollution is associated with the expansion of industrial projects (Carlson *et al.*, 2012), so they should be evaluated with stricter scientific criteria.

Another aspect to consider is that the adverse effects of mercury vary depending on its chemical form, concentration, and time of exposure, for example, the most toxic form of mercury is methyl mercury $[CH_3Hg]^+$ since it is absorbed by 90% compared to mercury chloride ($HgCl_2$) of which only 2% is absorbed (UNEP, 2003).

Lead

In birds of prey species that feed on rats and mice, in which case they have approached urban centers, it is more likely that the high levels of Pb detected in bones and feathers (Hunt, 2012) are related to sources of anthropic pollution. The case of the American Kestrel (*Falco sparverius*) (Figure 4) is one of the examples that are currently being worked on due to lethal concentrations of lead, especially due to the consumption of field mice and their relationship with pesticides in cultivated areas; the same happens with various species of owls (Figure 5) and tecolotes in Mexico since rodent hair that is expelled in the form of pellets (*i.e.*, regurgitation of material that was not degraded in the digestive tract of the bird and that can contain: bones, teeth, hair, feathers and diverse organic matter) is indicative and cumulative of heavy metals (McLean *et al.*, 2009).

In the case of the Conservation and Reintroduction Programs of raptors such as the White-headed Eagle (*Haliaeetus leucocephalus*), the solution since 2007 has been to change pellets or non-toxic bullets "lead-free" so that when accidentally ingested in carrion they do not cause harm, this is only part of the actions carried out in the legal hunting of mammals as sports trophies in the state of California USA. (Pagel *et al.* 2012).

Figure 4. Photograph of *Falco sparverius*, adult male individual, American Kestrel, Coyoacán City Hall, CD MX, the species is currently being studied for its Pb concentrations in blood, bones, feathers, and brain. Source: Own elaboration (2016)

Figure 5. Photograph of *Ciccaba virgata*, adult individual, Brown Owl, Municipality of Jalpan de Serra, Querétaro. Source: Own elaboration (2017)

Zinc

In birds such as the Osprey (*Pandion haliaetus*) (Figure 6), it has been considered that the normal physiological concentration is around 38 ppm in the liver, however, an updated record must be kept due to the high levels of Zn contamination in rivers, wetlands, lakes, and inland water bodies where this species feeds on fish probably with the presence of Zinc. Let us not forget that the availability of heavy metals is basically due to the geological history of the site where they are located or to the various anthropic activities, including irrigation with wastewater highly contaminated by heavy metals.

The high concentration of this metal causes the number of eggs per nest (*i.e*., clutch) to decrease, and particularly there is an abnormal growth of the bones of birds known as osteochondrosis (Martorell, 2009). Finally, this element is one of the most mobiles in the environment and is bioaccumulative (Zarazúa *et al*., 2013).

Figure 6. Photo of *Pandion haliaetus*, adult individual, Osprey, Ría Lagartos, Yucatán, may have high concentrations of Zn due to its strictly piscivorous diet. Source: Own elaboration (2014)

The Official Mexican Standard (SEMARNAP, 1996. NOM-001-ECOL-1996) establishes the maximum permissible limits of pollutants in wastewater discharges into national waters and goods, covers nine heavy metals and metalloids and the Official Mexican Standard (SEMARNAT/SSA, 2004. NOM-147-SEMARNAT/SSA-2004), which establishes criteria for determining the remediation concentrations of contaminated soils establishes 12 heavy metals; of which six were included in this documentary research work (As, Cd, Cr, Hg, Pb, and Zn) since they are part of studies related to birds of prey, the results are varied, although unfortunately an increase in the presence and concentration of heavy metals in water and soil is observed in most published works. In 90% of the verified studies, it is noted that the averages allowed for heavy metals in water and soils are well above the maximum permissible limits, this implies that there should be studies that monitor the routes followed by these chemical elements as well as their permanence in the environment and their potential effect on the health of flora and fauna.

CONCLUSIONS

In some cases, birds of prey exhibit non-lethal or sublethal levels of heavy metals, however, their continued evaluation may provide important future information and clarify long-term toxicological effects.

Although it is not a generality, various bird populations around the world are declining considerably, some of them possibly related to Climate Change or serious effects of environmental pollution.

This documentary research can be useful to analyze the migration of birds of prey from North America that converges on the route of mining and oil states such as Chihuahua, Guanajuato, Hidalgo, Querétaro, San Luis Potosí, Tlaxcala, Veracruz and Zacatecas and where the data for soil and water contamination are well above what is allowed in official Mexican standards. It is highly likely that the mining activity developed since colonial and oil times are the reasons why there are places that can be considered as sites of high exposure by heavy metals and metalloids in birds of prey. It is worth mentioning that this is not so different in northern countries such as the US and Canada due to their mining and oil history, plus the growing industry in all areas of development, with their clear consequences for flora and fauna.

In raptors, the results indicate that some birds increased their populations, others have remained constant, while others are in clear decline, therefore, conclusive studies on the subject would be lacking.

The proximity to urban, industrial, or agricultural areas can increase the concentrations of heavy metals in birds due to the feeding habits of each species. In some cases, such as in the Lerma River in the State of Mexico, low biodiversity has been recorded (Zarazúa *et al.*, 2013), possibly associated with high concentrations of heavy metals, since it is a site of discharge of water contaminated by industrial, agricultural and urban activities. It is also important to consider the persistence of heavy metals in nature and their intricate networks in ecosystems.

Undoubtedly, the information presented is a very reliable source that allows us to make decisions about heavy metal contamination in models such as birds of prey and establishes other doubts about what will happen to flora and fauna in the short, medium, and long term since their destiny is linked to our future.

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