Learned Discourse: Timely Scientific Opinions

Timely Scientific Opinions

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Submissions. All manuscripts should be sent via email as Word attachments to Peter M Chapman (peter@chapmanenviro.com).

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In a Nutshell...

Risk Assessment and Communication

The dangers of overestimating avian risks of pesticides, by Dwayne RJ Moore

Dangers include: loss of regulatory credibility; inability to focus decision making; and loss of important tools for agriculture.

Overstated risk conclusions: Wide-ranging mammals, by Lawrence V Tannenbaum

Overstating risk outcomes for wide-ranging mammals (putting aside that hazard quotients do not measure risk anyway) actually begins with wrongly including them in risk assessments.

The environmental trade-offs of human existence: Opening eyes wide shut, by Peter M Chapman

Human existence is based on trade-offs, all with some level of adverse environmental effects. We rarely consider these trade-offs; we live our lives with our eyes wide shut.

Atmospheric Contamination

What's in a butt? Environmental contamination from airborne cigarette butt emissions, by Mengyan Gong, Shahana Khurshid, and Dustin Poppendieck

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THE DANGERS OF OVERESTIMATING AVIAN RISKS OF PESTICIDES

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INTRODUCTION

Most pesticide uses result in exposure of aquatic life and wildlife because they are deliberately released to the environment to control weeds, pathogens, insects, rodents, and other pests. However, pesticides also provide substantial benefits to society and the environment including: improved yields for farmers and thus reduced prices for consumers; control of unwanted weeds in lawns and golf courses, along transit corridors and beneath power lines; control of invasive weeds in forests, wetlands, and other natural areas; protection of human health, livestock, and pets from disease-carrying organisms (e.g., diseases transmitted by mosquitoes, ticks, and fleas), and many others (Damalas 2009). The Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA) recognizes the risk–benefits balancing issue and thus requires all pesticides registered in the United States not to pose "any unreasonable risks to man or the environment, taking into account the economic, social, and environmental costs and benefits of the use of any pesticide."

As with many jurisdictions worldwide, the US Environmental Protection Agency (USEPA) conducts a risk–benefit analysis for each pesticide that is being considered for registration or reregistration. The USEPA assessments begin with the use of simple and conservative screening-level tools and, when required to better understand risk, move to the use of more sophisticated and refined tools. Refined risk assessments are most useful for pesticide use patterns and receptor groups with substantial benefits, where potential risks have been identified in screening-level assessments.

For the past decade, I have been involved in numerous pesticide assessments in the United States and elsewhere. With a few exceptions, it has been my experience that nearly all assessments, including those conducted by the USEPA, overestimate the risks of pesticides to aquatic biota and wildlife. That would be expected in screening-level assessments where the goal is to identify potential risk scenarios that require additional risk refinement. However, I have also found that refined risk assessments are also often guilty of grossly overestimating risk, even when all other lines of evidence point to a contrary conclusion. In this Learned Discourse, I present 2 recent examples of refined pesticide risk assessments that appear to have overestimated risks to birds. My focus is on birds, but the reality is that the overestimation of risk issue is a common issue across all receptors. I end by discussing 3 major consequences of overestimating risks of pesticides.

EXAMPLE 1

The USEPA recently released the draft biological evaluations for chlorpyrifos, diazinon, and malathion (USEPA 2016a, 2016b, 2016c). The purpose of the biological evaluations was to determine the risks of each of these pesticides to federally listed threatened and endangered species in the United States and their designated critical habitats. Remarkably, the draft biological evaluations found that chlorpyrifos and malathion are likely to adversely affect 97% of the 1596 listed species directly as well as 99% of their critical habitats. These biological evaluations (BEs) have undergone public comment and were recently finalized with no substantive changes to the original conclusions. Now that the BEs have been finalized by the USEPA, the consultation process will proceed to preparation of "biological opinions" by the US Fish and Wildlife Service and National Marine Fisheries Service. Following the release of the draft BEs, the headlines said it all:

"Two widely used pesticides likely to harm 97% of endangered species in US." [The Guardian, April 7, 2016]

"EPA: 97% of Endangered Species Threatened by 2 Pesticides. Causing a Meltdown of the Natural World." [InfoWars, April 12, 2016]

Sensationalism? Sure. However, despite years of work and enormous expenditures, the USEPA was only able to eliminate 3% of listed species as not likely to be adversely affected, and many of those were species that had already been extirpated or are currently presumed extinct. For nearly all listed species, the biological evaluation did not proceed beyond the use of highly conservative, screening-level risk assessment methods, likely explaining the high number of "likely to be adversely affected" conclusions. However, as shown below, in the few instances where refined assessment methods were used, risk was dramatically overestimated.

The USEPA conducted refined risk assessments for 13 listed bird species, including the Kirtland's warbler (*Setophaga kirtlandii*), an endangered migratory species that nests exclusively in young jack pine stands in Michigan and Wisconsin, and winters in the Bahamas. The USEPA's refined risk assessment for the Kirtland's warbler relied on the probabilistic Terrestrial Investigation Model (TIM) and Markov-Chain Nest Productivity Model (MCnest) to estimate acute and chronic risks, respectively. Despite being probabilistic, the models are highly conservative in many aspects with regard to determining the risks of chlorpyrifos and malathion to the Kirtland's warbler. For example, inputs to both models assume that Kirtland's warblers spend a significant portion of their foraging effort in and immediately adjacent to treated pastures during the breeding season. Decades of intense observation, however, have shown that these warblers only forage in young jack pine forests during the breeding season (FWS 2012). Other inputs used in TIM were also highly conservative. For example, the USEPA relied on the generic nomogram for terrestrial invertebrate residue levels, which is at least 4-fold higher than a chlorpyrifos-specific nomogram derived for foliage-dwelling invertebrates in orchards based on the results of well-conducted field studies (Moore et al. 2014). MCnest also assumes that if the conservative estimate of exposure exceeds the most sensitive avian reproduction no-observed-effect-level (NOEL), complete nest failure will occur rather than some partial response. Perhaps not surprisingly, given the combination of these and other conservative assumptions in TIM and MCnest, the models predicted greater than 80% mortality and near total reproductive failure for Kirtland's warblers annually for 2 of the 3 chlorpyrifos use patterns investigated. High acute and chronic risks were also predicted for malathion. No bird species, listed or otherwise, could withstand such catastrophic effects on an annual basis without going extinct. The reality is that the Kirtland's warbler has increased approximately 10-fold in abundance in recent decades despite widespread usage of chlorpyrifos and malathion (FWS 2012). This recovery was primarily due to intensive efforts to restore its favored jack pine habitat and removal of parasitic cowbirds from breeding territories (FWS 2012). The Fish and Wildlife Service recommended downlisting of the species from endangered to threatened in 2012 (FWS 2012).

EXAMPLE 2

The USEPA (2016d) recently released a preliminary Ecological Risk Assessment (ERA) for atrazine (this preliminary ecological risk assessment for atrazine has undergone public comment and is currently being revised; the schedule for finalizing the assessment is unknown). As with the refined avian assessment described in Example 1, the USEPA used TIM and MCnest to estimate acute and chronic risks of atrazine to birds. The models estimated significant mortality for many species and near total reproductive failure for small and medium omnivorous and insectivorous bird species (e.g., American robin, chipping sparrow, common yellowthroat, killdeer, and vesper sparrow) that forage in corn fields treated with atrazine (Figure 1). Even when an application rate well below the typical rates cited in USEPA (2016d) was modeled, near total reproductive failure was predicted. According to Table 6 of USEPA (2016d), 79.5% of atrazine applications to corn are at a rate higher than this low application rate in the United States. Approximately 60% to 70% of corn fields in the

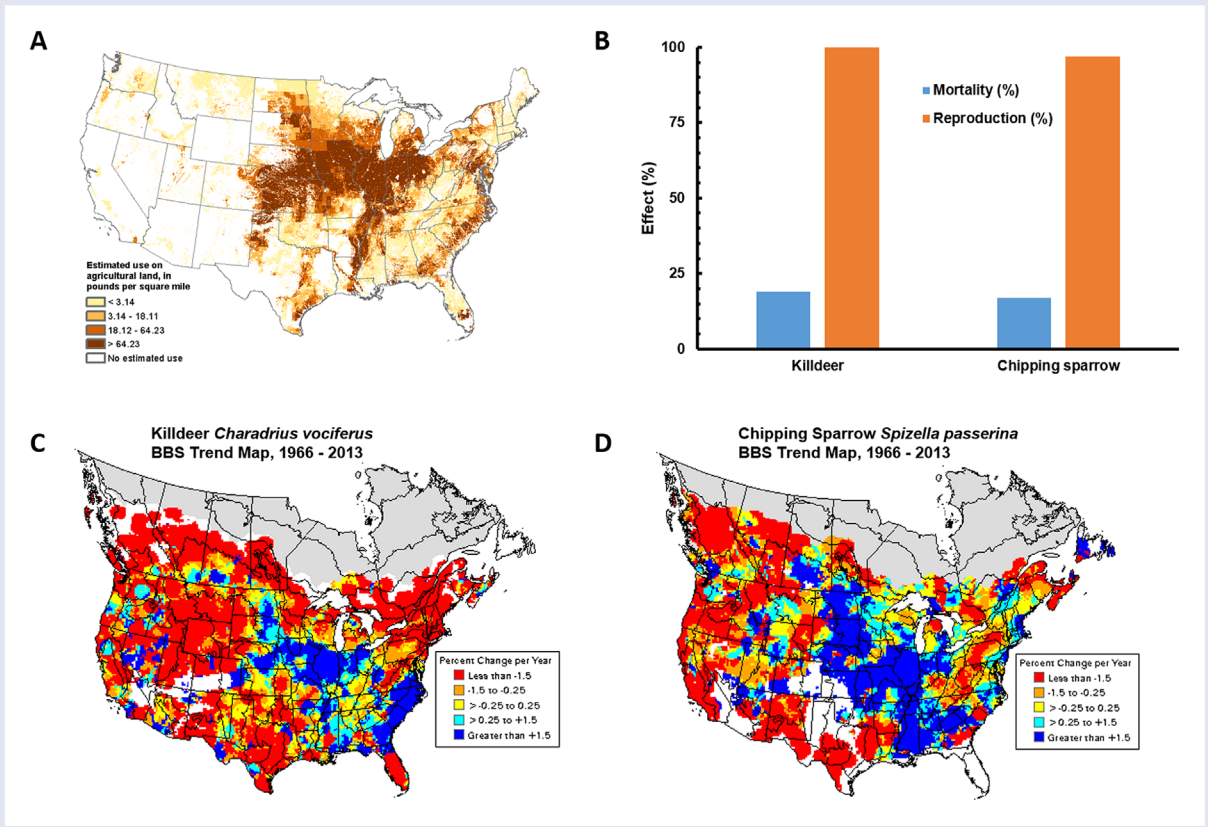

Figure 1. (A) Atrazine usage by crop reporting district (2006–2010) as reported in USEPA (2016d). (B) Estimated acute (i.e., mortality) and chronic (i.e., reduction in number of broods) effects of atrazine to killdeer and chipping sparrow from application of atrazine in corn at the maximum label rate according to TIM-MCnest. (C) USGS Breeding Bird Survey (BBS) trend map killdeer, 1966–2013 (Sauer et al. 2014). (D) USGS Breeding Bird Survey (BBS) trend map chipping sparrow, 1966–2013 (Sauer et al. 2014).

United States are treated with atrazine (see Table 4 of USEPA 2016d). Given the extensive acreage of the Midwest planted in corn and the risk predictions from TIM-MCnest, one would expect huge population declines of small and medium omnivorous bird species that forage in row crops in the Midwest. The risk estimates from TIM and MCnest, however, are misleading (see Olson et al. [2016] for additional information). First, despite atrazine having been one of the most widely used herbicides in the United States since being registered in 1959, the USEPA's own incident databases indicate only 1 probable incident involving a wild bird species (Canada goose) and a complete lack of avian incidents in the last 10 years. Second, many of the bird species predicted to be at significant risk from atrazine exposure have experienced strong and sustained population increases in areas where atrazine has been the most intensively used over the last 50+ years, while experiencing decreases in areas where atrazine use has been lower (Figure 1).

DISCUSSION

The issue of overestimated ecological risks is not unique to birds, nor is it unique to the USEPA's pesticide risk assessments. To be fair, pesticide assessments and biological evaluations are enormously complex undertakings typically involving many combinations of uses, formulations, application methods, regions, exposure pathways, and biota. In a world of limited resources and information, it is not always possible to perform highly refined assessments for each receptor at risk. That said, however, there are 3 obvious consequences to overestimating risks, particularly in high profile cases such as national endangered species assessments or for extensively used herbicides.

Loss of regulatory credibility

The pesticides mentioned in the examples ~~4 pesticides mentioned, hence my edits and same below~~ have been widely used for decades in the United States and have undergone assessment and reregistration by the USEPA on several occasions. What must the public think about an agency charged with protecting the environment suddenly finding that their assessment and registration process failed, on a grand scale, to protect nearly all listed species in the United States or bird communities in the Midwest? Even though the atrazine assessment is in draft form and may ultimately be revised, the damage to the USEPA's credibility with the public will be difficult to reverse.

Inability to focus decision making

It is possible that the pesticides mentioned are posing significant risks to some listed species or could affect certain receptors in parts of the United States. However, because these assessments were so conservative and risks significantly overestimated, we are at a loss to know how to focus risk mitigation

efforts. There are many possible risk mitigation measures with pesticides (e.g., in-field buffers, droplet size restrictions, prohibitions on application in sensitive areas, restrictions on timing of application). Choosing the optimal mitigation measures, given the benefits of the pesticide, requires a detailed understanding of risk. A finding that everything or nearly everything is potentially at risk is not helpful to the decision-making process.

Loss of important tools for agriculture

According to the National Corn Growers Association, farming without atrazine would cost corn farmers US$30 to US $59 per acre. Thus, its continued use saves US farmers up to US$3.3 billion per year and consumers up to US$4.8 billion per year. Atrazine is also an important tool for weed resistance management. Similarly, chlorpyrifos and malathion are important tools for controlling mosquito-borne disease vectors and dealing with insect resistance issues that arise with continuous use of single chemistries (e.g., pyrethroids or neonicotinoids).

There are, of course, many other consequences associated with overestimating pesticide risks. Clearly, time, effort, and resources must be invested in developing refined risk assessment tools and, when necessary, conducting refined assessments that generate a detailed understanding of pesticide risks. The sky, as it turns out, is not always falling.

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OVERSTATED RISK CONCLUSIONS: WIDE-RANGING MAMMALS

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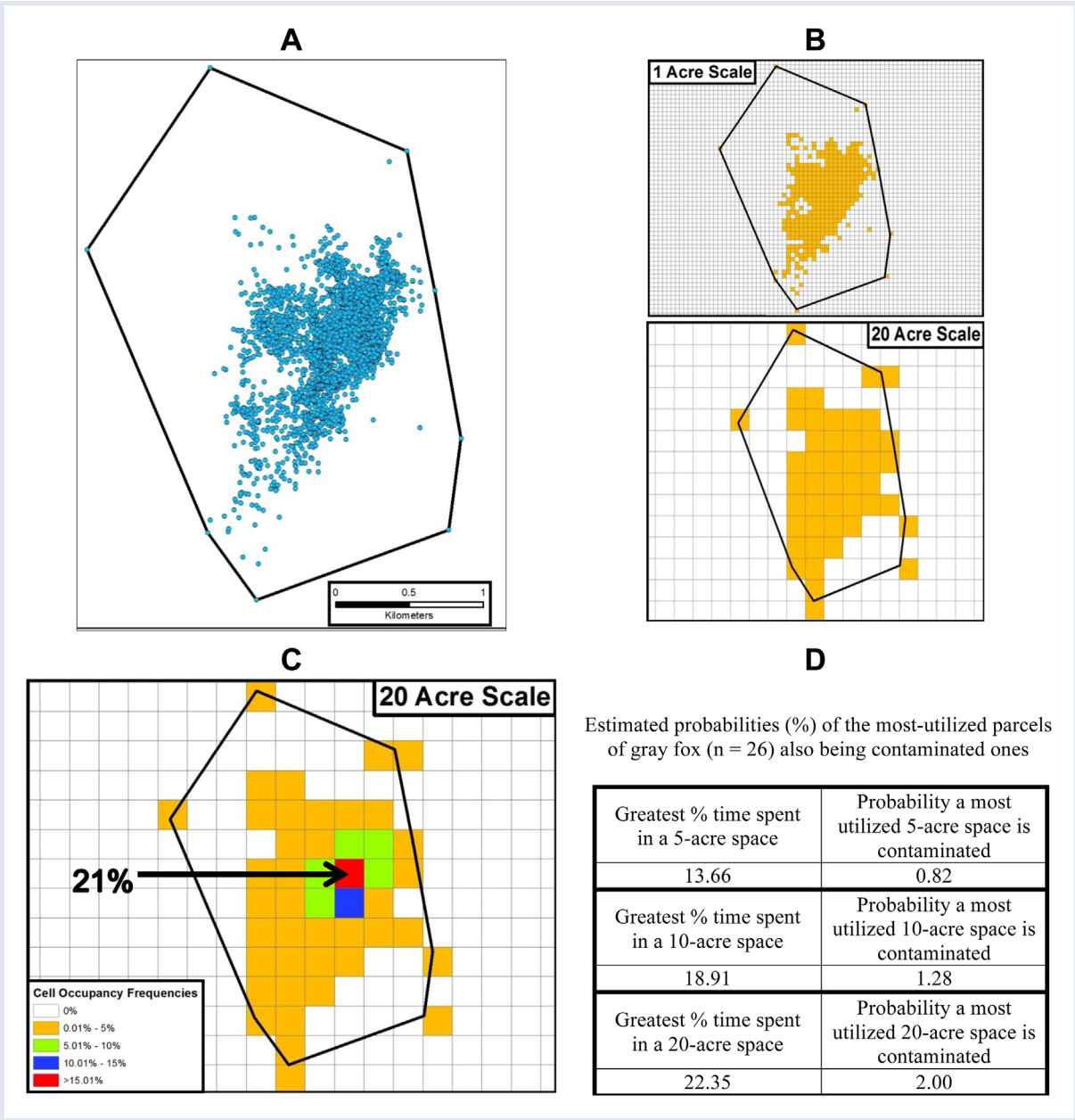
Ecological risk assessments (ERAs) routinely consider one or more wide-ranging mammals in their receptor-of-concern lists, with white-tailed deer (*Odocoileus virginianus*) and American red fox (*Vulpes vulpes fulvus*) perhaps the most commonplace examples. Because of the many frailties of ERA's hazard quotient (HQ) methodology, the most pronounced being that the HQ is not itself a risk expression (USEPA 1989; Tannenbaum 2013), these mammals stand an excellent chance of having failing HQs computed, paving the way for erroneous claims that they are at risk.

There is a lot more to this story, however, and it begins with a consideration of the sizes of contaminated sites. Although contaminated terrestrial sites that extend for several kilometers (such as mine tailings sites) do occur, these constitute a miniscule fraction of the contaminated sites in the United States and elsewhere. The overwhelming majority of sites, the ones to which this Learned Discourse pertains and the ones that so often populate the US National Priorities List (NPL), typically cover areas of only approximately 4 or 5 acres. A statistic lost on many is that some 60% of NPL sites, the United States' worst chemical actors, are 20 acres in size or less. Before wrongly assessing toxicity to deer, fox, and other wide-ranging mammals at typical contaminated sites, we would do best to put all HQ discussion aside—especially given the HQ's penchant for regularly exceeding 1.0 in site background—at least long enough to consider spatial realities.

Is it possible that a fox would spend enough time in a contaminated site, even one as large as say 20 acres, such that it would develop a toxicological endpoint of concern? The answer is a resounding "no"; a fox has a home range of 400+ acres. Furthermore, a fox has no choice but to abide by its preordained biologically dictated habits, and so each and every fox will necessarily cover that much turf in a month or 2. If ecological risk assessors have not yet stopped to consider the utter folly of the commonplace ERA practice of evaluating a fox at contaminated sites covering only a very small fraction of its home range and, worse, assuming it to spend 100% of its time there ("to be conservative, of course"), now is as good a time as any. We should not be so naïve as to think that a fox would allocate its time equitably over its 400+ acres; surely the habitat over such an expanse would not be uniform throughout, and some areas might seem more appealing to a fox than others. At the same time, we should not be so naïve as to expect, for example, that any few-acre parcel within the animal's 400+ acre home range (that could be a contaminated site) would garner 90% of the fox's time, leaving the fox to spend the remaining 10% of its time occupying the other

almost 400 acres of its home range. The time-allocation of mammals across their home ranges is never so heavily skewed.

We have the tools available to precisely know how wide-ranging mammals allocate their time over the terrain they cover. We should be highly desirous of such information, for it can illustrate whether or not an established receptor-of-concern selection criterion (Suter et al. 2000), high site fidelity, is being satisfied. Through work I have conducted with a team of wildlife experts, we have the hard numbers to demonstrate that white-tailed deer and gray fox (*Urocyon cinereoargenteus*), and by straightforward deduction, many more wide-ranging mammals, are wrongly considered in ERAs relative to contaminated sites that comprise only a very small fraction of their home range (Tannenbaum et al. 2013). Each captured animal was fitted with a GPS tracking collar programmed to record latitude and longitude (lat/long) locations as many as 16 times/day, and for periods of 6 months to a year while the animals were allowed to roam freely. At the end of the tracking period, the recorded lat/long locations were downloaded from the collars, contributing initially to a somewhat amorphous jumble of approximately 8000 dots in the case of deer, and approximately 2500 dots in the case of fox (see Figure 1A). The locations that describe the animal's total area used (TAU) were then overlain against a



Estimated probabilities (%) of the most-utilized parcels of gray fox (n = 26) also being contaminated ones

Greatest % time spent in a 5-acre space	Probability a most utilized 5-acre space is contaminated
13.66	0.82
Greatest % time spent in a 10-acre space	Probability a most utilized 10-acre space is contaminated
18.91	1.28
Greatest % time spent in a 20-acre space	Probability a most utilized 20-acre space is contaminated
22.35	2.00

Figure 1. (A) A gray fox's TAU (total area used; the black polygon border touching on the most outlying points of the cluster of lat/long locations). (B) Gridded TAUs at different scales (shaded cells are those that were occupied). (C) A gray fox's 1-year time-allocation map. (D) Probabilities of a fox's most-used area also being a contaminated area.

grid of uniform squares (or cells) of 1, 5, 10, or 20 acres, reflecting the sizes of almost all contaminated sites that are subject to ERAs (Figure 1B). The study design's singular assumption is quite reasonable: the percentage of each animal's total recorded locations that fall into a given cell (at any scale of analysis) is a reliable approximation of the percentage of an animal's time spent there. Only 1 additional spatial reality needs be taken into consideration before arriving at an answer to the pivotal question of whether a fox, deer, or any other mammal with a considerable home range spends enough time at a site to potentially be toxicologically challenged. It is the realization that contaminated sites do not occur frequently in the landscape. They do not occur every 400 acres or even every 3800 acres, the size of the average fox home range and TAU, respectively. The take-away point here is that, at most, there might be one contaminated site within any typical fox time-allocation map, such as is depicted in Figure 1C.

As Figure 1C shows for one profiled gray fox, indeed one 20-acre cell was observed to have been used more than any other. It is possible that the highlighted 20-acre cell that was occupied 21% of the time is a contaminated location. Before concluding that the animal tracking effort has furnished the support needed to justify a fox's inclusion in an ERA, we need to think again. Why would anyone want to assess a fox, or any animal for that matter, that is absent from a site of interest 79% of the time? What became of satisfying "the high site fidelity receptor-of-concern selection criterion"? If this is not enough to rule out the inclusion of fox from ERAs at most if not all sites (although it should be), there is another way to look at things.

What is the chance that a fox's most occupied 20-acre parcel would, coincidentally, be a contaminated site? The answer is 1% or less, and this is easily demonstrated. At most, there would be one contaminated site within a TAU. Divide 1, then (reflecting the singular hypothetical site) by the number of 20-acre parcels formed in the TAU gridding. Those who want to be conservative, can divide 1 by only those shaded cells in Figure 1C (i.e., the ones that had some fox occupancy, however minimal, although nonshaded cells in many instances, were undoubtedly also used). Figure 1D provides the mathematics for this exercise. And so, are we to assume that the most used/occupied cell within a fox's TAU (the one that might only garner as much as 20% of its time, do not forget) is coincidentally always the contaminated one?

This Learned Discourse emphasizes the reality that wide-ranging mammals will never be spatially relevant for study in ERAs. The take-home point is that overstating risk outcomes for wide-ranging mammals (putting aside that HQs do not measure risk anyway) actually begins with wrongly including them in ERAs altogether. Let us hope there comes a day when ERA matures to recognize that wide-ranging mammal consideration for conventional sites is so obviously pointless.

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THE ENVIRONMENTAL TRADE-OFFS OF HUMAN EXISTENCE: OPENING EYES WIDE SHUT

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Human existence is based on trade-offs, all with some level of adverse environmental effects. However, we rarely consider these trade-offs; in this regard, we live our lives with our eyes wide shut.

During a platform presentation at the 2016 Canadian Ecotoxicity Workshop (Edmonton, Alberta, September 25–28, 2016), I commented on the obvious reality that all human activities have effects; there are no neutral human actions. I pointed out that arguably the one human activity that has had the most environmental effect is food production, resulting in clearing of massive areas of land and animal habitat, and the planting of monocultures that typically require pesticides and fertilizers and that exclude their former inhabitants.

I provided an example adapted from Selck et al. (2017) of the extensive use of pesticides and fertilizers to grow potatoes on the east coast of Canada, pointing out that this is an ecosystem benefit to humans in terms of food production. However, I pointed out that this is also an ecosystem loss to humans in terms of food production because pesticides and fertilizers adversely affect spawning anadromous salmons in adjacent streams. Similarly in Costa Rica, the world's second largest producer of bananas, intensely farmed monocultures involving large applications of pesticides have resulted in significant transfers of pesticides and fertilizers into adjacent waterbodies, adversely affecting the resident biota (Syberg et al. 2017).

Another example is the use of salt on Canadian roads during the winter. Salt use reduces human injuries and deaths and, yet, salt also enters and has adverse effects on aquatic environments (Jones et al. 2017).

After I finished my presentation, I was asked if I had any advice as to how the general populace could be made aware of the consequences of trade-offs that provide for

human existence. It was an excellent question to which I had no good answer. With this Learned Discourse, I hope to begin the process of developing an answer, specifically opening eyes wide shut.

The arguably most significant trade-off of human existence is the power required for our civilization, which is primarily fossil fuel-based and whose extraction, processing, and use have a variety of environmental effects, most notably global climate change. Proponents of alternative energy sources (e.g., solar, wind, hydro, and geothermal) point out the environmental issues related to petrochemical energy but ignore those related to alternative energy sources. For instance, in my Canadian province of British Columbia, work has begun on the Site C Dam, which will provide a large amount of "clean" hydroelectric power. Construction of that dam will drown extensive areas of land that presently provide ecosystem services such as food production, habitat, and cultural services. Proponents and opponents of the Site C Dam keep their eyes wide shut and ignore the possibility of a middle ground.

Activists denounce construction of oil pipelines yet rely on petroleum products to get to demonstrations and for most aspects of their daily life. They provide environmental arguments. Some are cogent and reasonable; some are disingenuous and ideological opposition. Similarly, proponents of oil pipelines provide economic arguments. Some are cogent and reasonable; some are dissimulating spin and ideological support. Again, the eyes are wide shut.

Birth control pills help reduce human populations, yet the residues that leave women's bodies and are released to aquatic environments from sewage treatment plants cause feminization of male fish. We develop new drugs to further the health of humans and domestic animals and livestock, but these often have unintended consequences. For instance, diclofenac, a "wonder drug" used to treat pain and inflammation in humans and cattle, proved to be toxic to vultures; vulture populations in India have been reduced by 99% with consequent increase in rabies in humans because vultures prey on rabid dog populations (http://qz.com/700998/india-has-a-grand-plan-to-bring-back-its-vultures/).

There are no clear solutions to the difficult trade-offs made to support human existence but, with our eyes wide shut, we will not even accept the possibilities of trade-offs, of informed eyes-open choices. Global climate change is projected to impose dramatic environmental changes and is clearly enhanced by human activities. However, with the Earth's present and increasing population, and increasing demands from the populations of developing countries for the same energy benefits as in developed countries, it is not reasonably possible at the present time to totally stop using fossil fuels. Furthermore, alternative energy sources carry their own environmental impacts. Wind energy interferes with scenic landscapes, and bats and birds are often at risk from the spinning turbine blades. Solar power poses similar risks to birds in areas where solar collectors are concentrated.

The bottom line is that all humans, no matter how well intentioned and how much they try not to, cause adverse effects to the environment to sustain themselves. Those adverse effects have increased with population size and use of resources (affluence is proportional to resource use) (Wang et al. 2016). This is a reality we need to see before we can deal with it.

Accepting that all human activity conveys both positive benefits and negative effects, we need reliable and accurate approaches to quantify the consequences of different human activities, and evaluate the ensuing trade-offs to determine those actions that provide the greatest overall benefits both to us and to the environment. We need to use appropriate means to enhance those benefits. For instance, the adverse effects of pesticides and herbicides used on crops could be ameliorated by genetically engineering crops for disease and pest resistance; plant hybridization has a long history in agriculture and gardening. Moreover, genetic engineering has the potential to both reduce, for example, adverse environmental effects to fish and other biota related to agriculture and increase food production for human use. Organic farming may have a role in farming, but it is not the only solution (e.g., https://blogs.scientificamerican.com/science-sushi/httpblogsscientificamericancomscience-sushi20110718mythbusting-101-organic-farming-conventional-agriculture/). Yet to too many of us, genetically engineered crops are anathema; only organic farming is acceptable even though, if all farming were organic, there would be mass human starvation because we would not be growing enough food.

We need to open eyes wide shut. For example, rather than denouncing the use of oil as evil, let us recognize that we still need fossil fuels while working to minimize their use and their potential adverse environmental effects. Pipelines are a safer means of transporting oil than by rail, yet pipelines seem to be the sole focus of eyes wide shut environmental activists.

As I said at the start, this Learned Discourse only hopes to start the process of opening eyes wide shut to the trade-offs that provide for human existence. I ask for input both directly and via Letters to the Editor or Learned Discourses to this journal. We cannot continue with eyes wide shut—how do we start to open them to the ultimate benefit or both ourselves and our environment, before it is too late?

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WHAT'S IN A BUTT? ENVIRONMENTAL CONTAMINATION FROM AIRBORNE CIGARETTE BUTT EMISSIONS

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Cigarette butts are ubiquitous in the environment. Globally, 5 trillion cigarette butts are generated every year (Smith and Novotny 2011). Cigarette butts are one of the most common forms of litter discarded onto beaches, bus stops, roads, streets, parks, and many other public places (Novotny et al. 2011). They are also commonly found in ashtrays in homes, cars, and public places (Novotny et al. 2011). Most cigarette filters (a major part of cigarette butts) are made of cellulose acetate, which is photodegradable, but not easily biodegradable (Puls et al. 2011). Hence, they may persist in the environment for more than 10 years. Although many measures have been taken to prevent or mitigate cigarette butt pollution, none have been effective (Smith and Novotny 2011).

More important than being unsightly litter, chemicals can emit or leach from cigarette butts and impact human health and the environment. Instances of children ingesting cigarette butts have been reported, which can cause toxic effects, including vomiting within 20 min (Novotny et al. 2011). The impacts of cigarette butts on animals have been reported more widely, for example, genotoxicity in house finches that use cellulose acetate as lining material in nests, shorter life span and higher mortality rates during developmental stages for mosquitos that have hatched in water contaminated by cigarette butts, as well as mortality and behavioral modifications in snails exposed to cigarette butt leachate in seawater (see references within Poppendieck et al. [2016]).

Given the ubiquitous nature of cigarette butts and the potential for causing adverse environmental impacts, a literature research was conducted to review studies on cigarette butt airborne emissions using Web of Science and Compendex Engineering Village databases with "cigarette butt*," "cigarette filter*," "cigarette tip*," and "tobacco filter*" as keywords in January 2016. Combining search results from the 2 databases, 2381 articles were identified. A detailed review of these articles has been published by Poppendieck et al. (2016). In summary, none of the 2381 articles studied airborne emissions from cigarette butts under typical indoor or outdoor environment conditions. Four articles reported the emission of chemicals from cigarette butts into headspace vials at elevated temperatures (>80 °C). However, the results of these studies cannot be translated to real environments because the high temperatures may result in the emission of chemicals that are not likely to be emitted under normal indoor or outdoor conditions. Therefore, the mass of chemicals emitted in these studies cannot be used to calculate emission rates. Four of the reviewed articles studied the chemical emission rates from cigarette butts into water and showed that these emissions can be a short-term phenomenon. Moerman and Potts (2011) reported that more than half of the metals in cigarette butts were leached within 1 day in aqueous solutions. In addition, 22 articles measured chemicals retained in cigarette butts using solvent extraction methods. These studies describe the kinds of chemicals retained in cigarette butts but not the chemical emission rates into the environment.

The chemicals reported in these 30 articles from cigarette butt emission and extraction studies are summarized in Table 1, and include alcohols, alkaloids, aromatic amines, carbonyls, hydrocarbons, insecticides, metals, nitrosamines, nitro polycyclic aromatic hydrocarbons, polycyclic aromatic hydrocarbons, phenols, phthalates, pyrazines, pyrroles, terpenes, and terpenoids. Generally, each study only examined a small number of chemicals. Approximately 130 chemicals have been reported to be present in cigarette butts. These chemicals are not unique to cigarette butts and are often the same chemicals detected in mainstream smoke and sidestream cigarette smoke. However, many more chemicals (40 000–100 000) (Dalluge et al. 2002) have been identified in cigarette smoke, some of which could potentially be retained in cigarette butts and subsequently emitted into the environment depending on the environmental conditions and chemical properties.

Overall, cigarette butt emissions are just beginning to be understood, with more comprehensive studies needed to examine the extent of these emissions. These emission rate studies need to cover a wide range of chemicals, with a focus on chemicals with higher toxicity. In addition, studies are needed to quantify changes in emission rates over time under different conditions. These studies will be challenging due to the different emission characteristics of the chemicals and the variety of influencing factors that can affect emissions from cigarette butts, such as brand, filter material, butt length, degradation, ambient temperature, airflow around the cigarette, ventilation through the cigarette, number of puffs drawn, and smoking method.

Given the lack of information on airborne emissions from cigarette butts under typical indoor or outdoor conditions, we conducted some preliminary experiments to measure the emissions from cigarette butts in headspace vials. A freshly generated cigarette butt and a cigarette butt aged on the ground for an unknown period of time were incubated in headspace vials at 35 °C (this temperature is closer to ambient conditions than headspace temperatures in previous studies). The vials were then sampled with Tenax-TA tubes and analyzed using gas chromatograph-mass spectroscopy (GC-MS). Both cigarette butts emitted more than 100 chemicals. For the freshly generated cigarette butt, the chromatogram peaks with the top 5 largest areas were identified as d-limonene, toluene, pyridine, benzene, and styrene. For the cigarette butt found on ground, the top 5 peaks were different from the

Table 1. Summary of chemicals detected in cigarette butt emission and extraction studies[a]

Media	Nr of papers	Chemical groups detected	Chemical names
Air	4	6 alcohols	ethanol, 2-furfuryl alcohol, isopropanol, methanol, 1-methoxy-2-propanol, 1-ethoxy-2-propanol
		21 carbonyls	acetol, acetone, butyl acetate, cyclohexanone, 2-pentanone, n-propanol, n-propyl acetate cyclopentanone, 2-cyclopentenone, 2-methylcyclo pentenone, 4-methyl-2-pentanone, methyl n-butyl ketone, n-butyl alcohol ethyl acetate, 3-furaldehyde, 2-furaldehyde, isopropyl acetate, protoanemonin, acetol formate, 3-methyl-2-cyclopentenone, 2,3-pentanedione
		11 hydrocarbons	ethyl benzene, benzene, 3,3-dimethyl-1-butene, pyridine, cyanobenzene, cyclooctatetraene, isocapronitrile, toluene, p-xylene, m-xylene, o-xylene
		2 pyrazines	pyrazine, 2-methylpyrazine
		4 pyrroles	n-methylpyrrole, pyrrole, 3-methylpyrrole, 2-methylpyrrole
		1 terpene	limonene
Water	4	1 alkaloid	7-carbaldehyde camptothecin
		7 aromatic amines	nicotine, hexaconazole, imidocarb, cotinine, 2-(pyridin-3-yl) pyrrolidine-1-carbaldehyde, sulfadoxine, 5-(4,6-dichloropyridin-3-yl)-pyridine-1(2h)-carboxamidea
		2 carbonyls	5-(4-hydroxy pyridin-3-yl)-pyridine-1(2H)-carboxamide, 7-keto-benzo(a)pyrene
		8 metals	aluminum, barium, cadmium, lead, manganese, nickel, strontium, titanium
		1 nitrosamine	N-nitrosonornicotine
		1 PAH[b]	benzo(a)pyrene
		3 phenols	rutin, 2,2-dimethyl-2,3-dihydrobenzofuran-7-ol, 1,5-dihydroxy-anthraquinon
		2 terpenes	beta-carotene-4,4′-dione, xanthophylls
Solvent	22	8 carbonyls	acetone, formaldehyde, acetaldehyde, acrolein, propionaldehyde, crotonaldehyde, 2-butanone, butyraldehyde
		3 insecticides	maleic hydrazide, chlorantraniliprole, imidacloprid
		1 metalloid	arsenic
		8 metals	cadmium, chromium, copper, mercury, iron, lead, manganese, zinc
		1 nitrosamine	TSNAs[d,e]
		3 NPAH[c]	1,3-dinitronaphthalene, 9-nitroanthracene, nitrobenzene
		6 PAHs	anthracene, benzo[a]pyrene, benz[a]anthracene, benzo[b]fluoranthene, fluoranthene, pyrene
		8 phenols	catechol, hydroquinone, m-cresol, o-cresol, p-cresol, phenol, resorcinol, rutin
		3 phthalates	dibutyl phthalate, diisobutyl phthalate, di(2-ethylhexyl) phthalate
		1 terpenoid	solanesol

[a]The citations can be found in Poppendieck et al. (2006).
[b]PAH = Polycyclic aromatic hydrocarbons.
[c]NPAH = Nitro polycyclic aromatic hydrcarbon.
[d]TSNAs = Tobacco-specific nitrosamines.
[e]The specific chemicals of TSNAs are not available in the cited paper.

freshly generated butt: nicotine, 3-methyl-pyridine, furfural, pyridine, and methyl-pyrazine. The results indicated that short-term and long-term emissions from cigarette butts may differ, and different chemicals need to be considered at different stages of emission. Note that these 2 butts are only used to investigate methods and get a preliminary idea on the cigarette butt airborne emission and are not necessarily representative of all the cigarette butts in the real world. For further study, more cigarette butts will be measured and we will quantify airborne emissions of selected chemicals from cigarette butts using headspace analysis after they have been exposed for specific periods of time to a variety of environmental conditions. This will enable us to examine the influence of temperature, relative humidity, surrounding flow rate, photodegradation, and water content on airborne emissions from cigarette butts.

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Disclaimer—Certain trade names or company products are mentioned in the text to adequately specify the experimental procedure and equipment used. In no case does such identification imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the equipment is the best available for the purpose.

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