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Part 1.2

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Human-mediated shifts in animal habitat use: Sequential changes in pronghorn use of a natural gas field in Greater Yellowstone

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ABSTRACT

To manage America's 991,479 km^2 (245 million acres) of public BLM lands for such mixed uses as natural resource extraction, wildlife, and recreation requires knowledge about effects of habitat alterations. Two of North America's largest natural gas fields occur in the southern region of the Greater Yellowstone Ecosystem (Wyoming), an area that contains >100,000 wintering ungulates. During a 5-year period (2005–2009), we concentrated on patterns of habitat selection of pronghorn (*Antilocapra americana*) to understand how winter weather and increasing habitat loss due to gas field development impact habitat selection. Since this population is held below a food ceiling (i.e., carrying capacity) by human harvest, we expected few habitat constraints on animal movements – hence we examined fine-scale habitat use in relationship to progressive energy footprints. We used mixed-effects resource selection function models on 125 GPS-collared female pronghorn, and analyzed a comprehensive set of factors that included habitat (*e.g.*, slope, plant cover type) and variables examining the impact of gas field infrastructure and human activity (*e.g.*, distance to nearest road and well pad, amount of habitat loss due to conversion to a road or well pad) inside gas fields. Our RSF models demonstrate: (1) a fivefold sequential decrease in habitat patches predicted to be of high use and (2) sequential fine-scale abandonment by pronghorn of areas with the greatest habitat loss and greatest industrial footprint. The ability to detect behavioral impacts may be a better sentinel and earlier warning for burgeoning impacts of resource extraction on wildlife populations than studies focused solely on demography. Nevertheless disentangling cause and effect through the use of behavior warrants further investigation.

1. Introduction

One of America's most vexing and polarizing challenges is how best to manage the 991,479 km^2 (245 million acres) of Bureau of Land Management (BLM) public lands established for multiple uses such as natural resource extraction, wildlife, and recreation. The intersection between energy development and biological conservation affords opportunities both to gather knowledge and to implement findings about how to mitigate impacts to wildlife. As the footprint of human development continues to expand globally into regions that have historically supported abundant wildlife resources, there will be even more pressing needs for long-term data sets, in conjunction with baseline data, to examine changes in life history parameters and behavioral processes.

Western North America contains abundant natural resources, including wildlife populations that still undergo spectacular processes like long-distance migration, a globally-imperiled ecological phenomenon (Berger et al., 2006). Unfortunately, conflicts often arise because the harvest of natural resources is not always compatible with maintaining wildlife populations, thus necessitating choices. These decisions are often contentious because interest groups have vastly different priorities. This puts policy-makers and wildlife managers in the position of needing to make informed decisions about trade-offs, as they attempt to balance the needs of wildlife against people's desire for energy independence. Ecological theory can guide policy-makers and wildlife managers. For instance, we know from studies based on carrying capacity theory, that a reduction in habitat will ultimately lead to a decline in population size, or when extreme a local extirpation. However, because carrying capacity is not static, and is determined by the complex interplay of many factors (*e.g.*, weather, human-footprints on the landscape), identifying thresholds is difficult. Often the challenge is further complicated by a lack of baseline data on wildlife populations' behavior or demography against which to assess short-term fluctuations.

Large-scale natural resource extraction has the potential to impact animal movements, habitat use and associated behavior, demography, and population trends (*e.g.*, Bradshaw et al., 1997;

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Joly et al., 2006; Sawyer et al., 2006; Vistnes and Nellemann, 2008), that includes such North American icons as, caribou (*Rangifer tarandus*; Bradshaw et al., 1997; Cameron et al., 2005; Noel et al., 2004), greater sage grouse (*Centrocercus urophasianus*; Copeland et al., 2009; Walker et al., 2007), and mule deer (*Odocoileus hemionus*; Sawyer et al., 2009). At a broader scale, effects of natural resource extraction span all continents and ecosystems and vary from deserts to tropical forests and polar regions (Contreras-Hermosilla, 1997; Joly et al., 2006; Peres and Lake, 2003).

How wildlife populations respond to increasing human-footprints and habitat loss in the form of energy infrastructure is oftentimes determined primarily by how close the population of concern is to its food ceiling (i.e., carrying capacity; see Stewart et al., 2005). If, for example, a population approaches its habitat's food ceiling, then impacts of habitat loss and fragmentation may be immediately revealed through either behavior (i.e., habitat or resource selection patterns) or demographic (*e.g.*, changes in survival) responses or both simultaneously. Further, if a population is maintained below its food supply by harvest but its' habitat is substantially squeezed or fragmented over time, it seems reasonable to expect changes in its spatial ecology even if sufficient food remains available. Mule deer, for example, respond to energy footprints although presumptively held below a given habitat's food resources (see Sawyer et al., 2009). With respect to the Upper Green River Basin (UGRB) in western Wyoming, we explored the extent to which increasing energy development affected several correlates of pronghorn (*Antilocapra americana*) biology with a specific emphasis on spatial ecology. Beyond habitat loss and human harvest however, weather exerts strong direct effects on animal movements (Hebblewhite et al., 2005). For species like pronghorn, deep snow may exacerbate risks brought on by habitat loss associated with energy field development.

Two of the largest gas fields in the lower 48 USA (i.e., the Pinedale Anticline Project Area (PAPA) and Jonah Fields, see Fig. 1) occur in the wintering home range of America's longest terrestrial migrant – pronghorn of the Greater Yellowstone Ecosystem (Berger et al., 2006). This is significant because Wyoming contains an estimated 400,000 of the world's approximately 700,000 pronghorn and the UGRB herd represents one of the largest in the state (Grogan and Lindzey, 2007; Hoffman et al., 2008).

Our primary study questions are therefore aimed at understanding the interplay of snow and industrial development on habitat selection by pronghorn in this area of extreme energy development. Given that pronghorn are likely kept below their food ceiling (see Stewart et al., 2005) through annual harvest of a mean of 2477 ± 701 pronghorn (*e.g.*, from 2001 to 2009 in Hunt Units 86–91 in the Sublette Herd in the Upper Green River Basin; Wyoming Game and Fish Department, unpub. data), we expected habitat to be a non-limiting factor. If true, then observed resource selection responses of pronghorn to gas field infrastructure may fall below detectable levels (Fig. 2). This annual level of harvest for these six hunt units is over a 4000 km^2 area where we conducted monthly distribution flights during the winters of 2005–2010 for which we never counted more than 6500 total animals (unpub. data). As a consequence, we assume that such relatively high human harvest maintained pronghorn below a point at which body condition would be affected by intra-specific competition for food. On the other hand, variation in snow depth in the UGRB and elsewhere (Martinka, 1967) is a key driver of winter movements and food availability. Consequently, we hypothesized that an increasing human-footprint from gas field development over time would sequentially lower the food ceiling through habitat loss independent of effects of snow depth. Our conceptualized interactions among snow, human harvest, and energy-induced habitat loss are depicted in Fig. 2.

There are two general predictions that stem from current BLM and industry proposals to reduce native habitats by 5–14% (BLM, 2006, 2008): (1) given the harvest-related limitations on population size, the UGRB landscape will retain enough crucial winter range and therefore pronghorn will respond in ways reflecting no biological impacts (i.e., patterns of resource selection will not vary), or (2) pronghorn will show heightened sensitivity to increasingly degraded habitats (i.e., pronghorn will avoid or select against areas in which density of well pads and roads have exceeded a threshold). These dual scenarios enable opportunities to examine fine-scale movements in relation to progressive habitat change while accounting for effects of snow and other variables.

To understand pronghorn use of winter range, we estimated both individual- and population-level resource selection responses to habitat loss, fragmentation, and human activity associated with gas field development and infrastructure using mixed-effects resource selection function (RSF) models to determine which factors influence pronghorn habitat use in gas fields during winter. Further, we examined pronghorn response to gas field development over a 5-year time frame to understand how varying and increasing densities and scale of development and infrastructure impact pronghorn habitat use on their crucial winter range.

2. Methods

2.1. Study area

The primary study area within the UGRB was the PAPA and Jonah gas fields (Fig. 1) where elevations range from 2100 to 2800 m. The larger of the two gas fields is the 80,127 hectare (198,000-acre) region designated as the PAPA, while the smaller 12,140 hectare (30,000-acre) Jonah Field is adjacent to the PAPA to the south (Fig. 1). At the end of 2009, 1713 wells had been drilled in the PAPA and 1623 wells had been drilled in the Jonah. However, less than 3% of the physical habitat in the PAPA and 14.3% of the habitat in the Jonah boundary areas are currently disturbed by roads and well pads (BLM, 2008). The BLM has approved the drilling of 1500 new wells inside the PAPA and 3100 additional new wells inside the Jonah (BLM, 2006, 2008). The infrastructure in the PAPA is projected to continue with expansion of well pads, roads, and pipelines through 2023, drilling through 2025, and production through 2065 (BLM, 2008). In the Jonah, 250 wells will be put into production each year over a period of 76 years up to a maximum of an additional 3100 wells (BLM, 2006).

The UGRB represents the southern reaches of the Greater Yellowstone Ecosystem, where species such as pronghorn migrate from summer range in areas as far away as Grand Teton National Park (150 km distance) to their winter range in the UGRB (Berger et al., 2006; Sawyer and Lindzey, 2000; Sawyer et al., 2005). This region consists primarily of sagebrush (*Artemisia* spp.) steppe communities in rolling hills punctuated by occasional plateaus. The sagebrush steppe in this region has a strong spatial pattern linked to topography (Burke et al., 1989). The topography also leads to snow being swept off of the higher elevation plateaus of the region by wind providing crucial winter range for some estimated 100,000 ungulates such as pronghorn, mule deer, and elk (*Cervus elaphus*) (Berger et al., 2006; Burke et al., 1989; Sawyer et al., 2009). Primary statutory authority for land and habitat management is the Bureau of Land Management (BLM), who also oversees access to minerals in the UGRB. The region around the New Fork River in the PAPA has been formally designated by the WGFD as crucial winter range for pronghorn for longer than the past 50 years (Fig. 3).

2.2. Animal capture and handling

Through our 5-year study duration, we captured and collared 125 adult ($\geqslant$1.5 years of age) female pronghorn inside the two gas fields

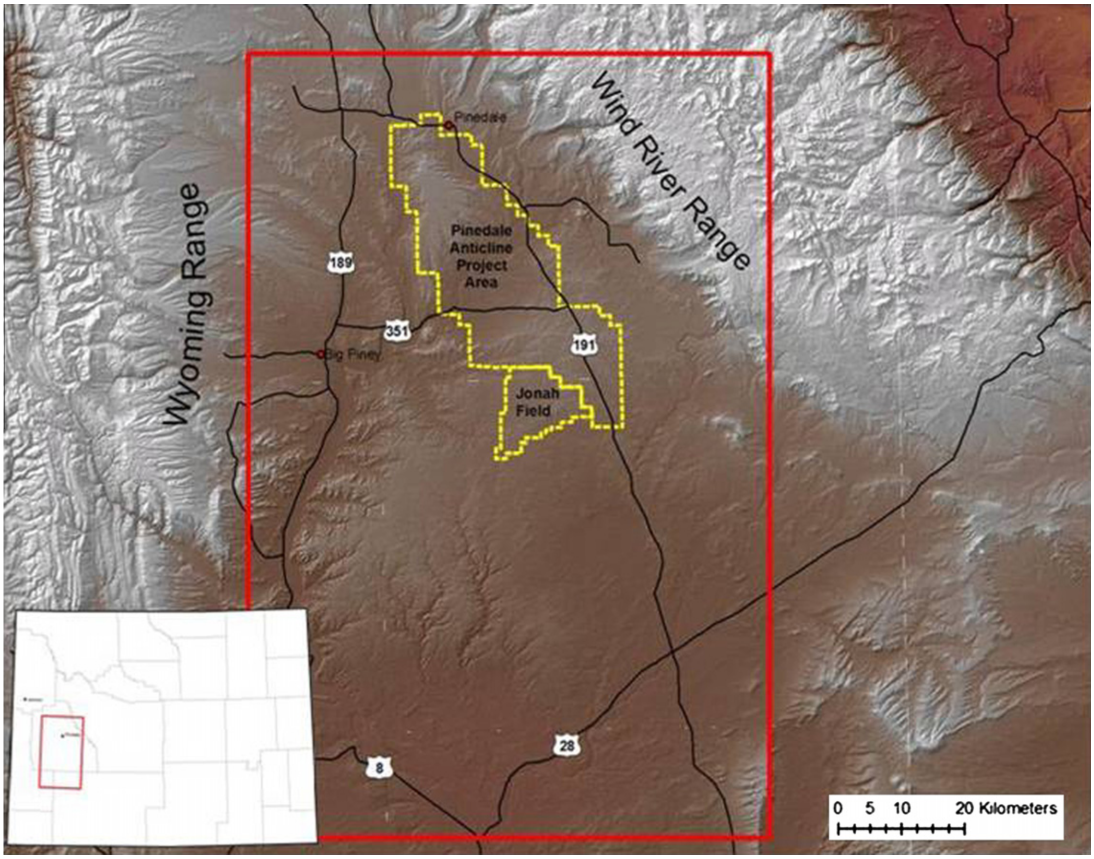

Fig. 1. Location of the Upper Green River Basin in the Greater Yellowstone Ecosystem of western Wyoming. The two largest natural gas fields in the lower 48 states of the USA, the PAPA (northern outline) and Jonah (southern outline) fields are highlighted.

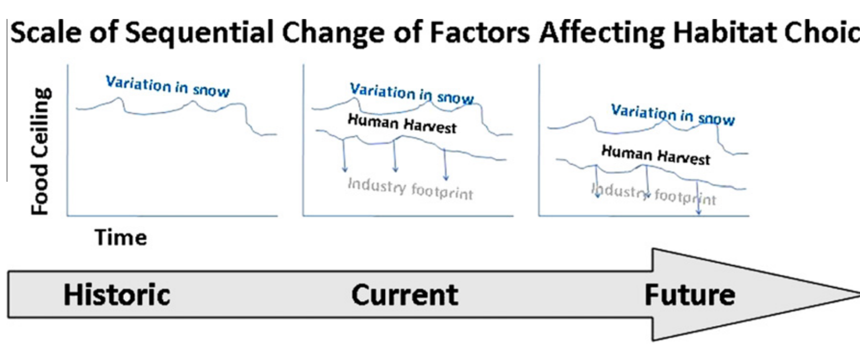

Fig. 2. Conceptual diagram demonstrating how carrying capacity (i.e., food ceiling) for pronghorn during winter might be affected by varying snow depth. Habitat loss and fragmentation by an increasing human-footprint due to natural gas field development over time lowers the food ceiling. However, relatively high levels of human harvest of pronghorn that keeps the population below the food ceiling may potentially mask the true impacts of a further lowering of the food ceiling due to energy infrastructure.

using a net-gun fired from a helicopter. We manually restrained females and fitted each female with a global positioning system (GPS) collar with 8-h mortality sensors and remote release mechanisms (Advanced Telemetry Systems, Isanti, MN). The GPS collars were programmed to collect eight locations per day during winter and migratory periods (1 January–15 May; 16 October–November 15), and a single location per day during summer and early fall (16 May–15 October). All handling was in accordance with Institutional Animal care protocols established by the Wyoming Game and Fish Department and the American Society of Mammalogists.

2.3. Habitat loss

During the 5-year study, sequential changes in the proliferation of roads, well pads and surface disturbance inside the gas fields in the UGRB occurred as natural gas wells were drilled (see Fig. 4 for example). We used 10 m resolution SPOT satellite imagery to calculate habitat loss from construction of well pads and roads in the PAPA and Jonah Field. The satellite image was displayed onscreen and roads and well pads were hand-digitized. The base data layer of roads and well pads from 2005 to 2009 was obtained from the Pinedale, Wyoming, office of the BLM. The BLM's dataset was digitized from 0.6 m resolution imagery at a scale of 1:2000. New roads and well pads constructed each year since the BLM's data were last updated were then added to the existing shapefile for each year's modeling effort. New roads consisted of any identifiable two-tracks, improved dirt, or paved surfaces. Any two-track that was not apparent from the satellite image was not digitized. Well pads were denuded areas used to house gas field structures of any kind that had identifiable roads leading to them. Well pads

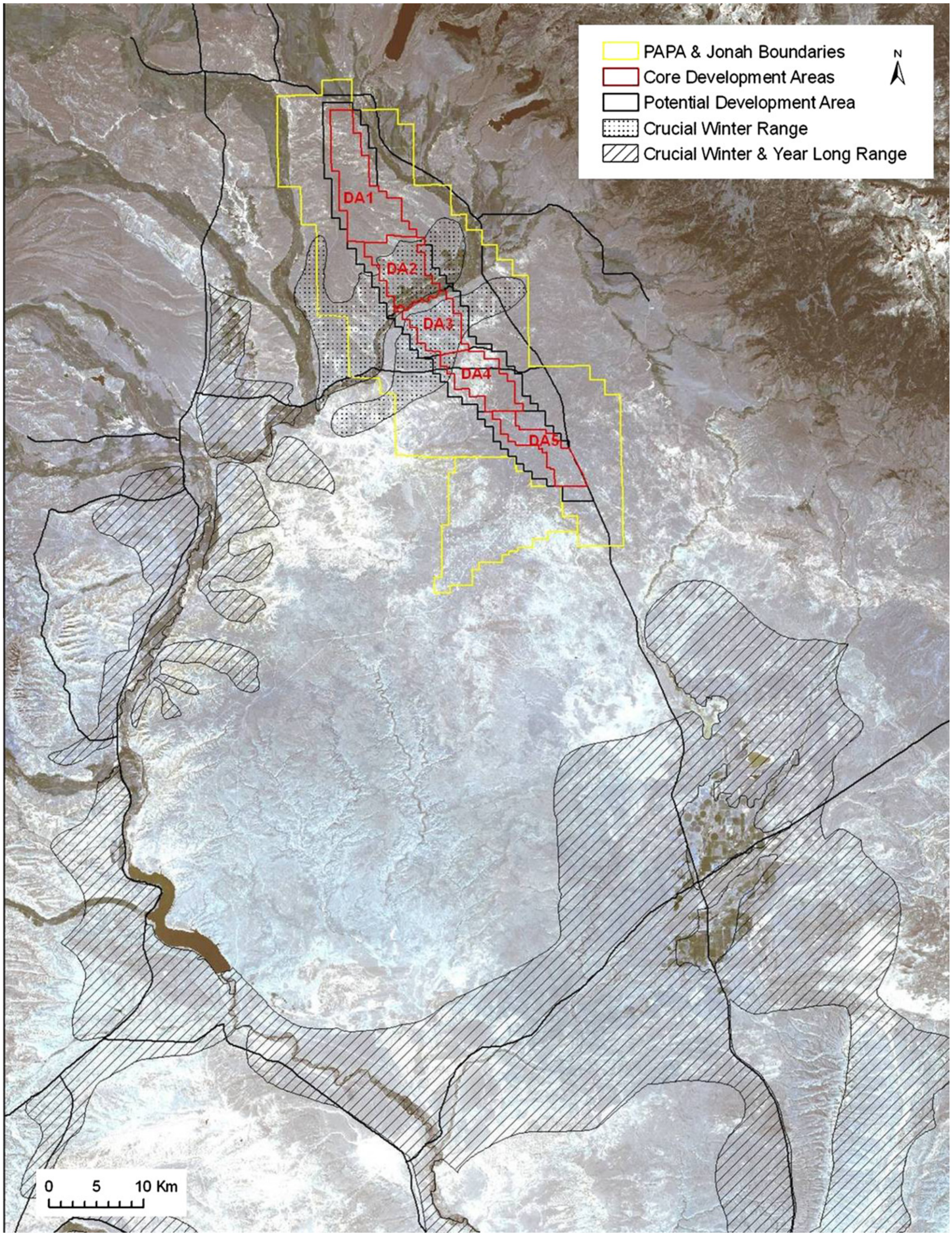

Fig. 3. Wyoming Game and Fish Department crucial winter and year long range designations for pronghorn of the UGRB. PAPA Core Development Areas 2 and 3 (DA2 and DA3) and the proposed Potential Development Area overlap extensively with designated crucial winter range.

were treated the same as pumping stations, equipment storage facilities, etc. ArcMap 9.3 (Environmental Systems Research Institute, Redlands, CA) was then used to calculate the total area of habitat loss from construction of roads and well pads for all years.

We utilized a grid-based method to assess habitat loss associated with construction of roads and well pads for each year from 2005 to 2009. To determine the proportion of disturbed habitat, we first overlaid the boundaries of the PAPA and Jonah Field with a grid comprised of 300 m $\times$ 300 m cells. We used 300 m because this was the median distance between pronghorn locations and well pads in winter 2005–2006 based on location data collected using GPS collars; thus, 300 m appeared to be a plausible distance at which pronghorn responded to objects in their environment. Similarly other species, such as mule deer, likely respond and make

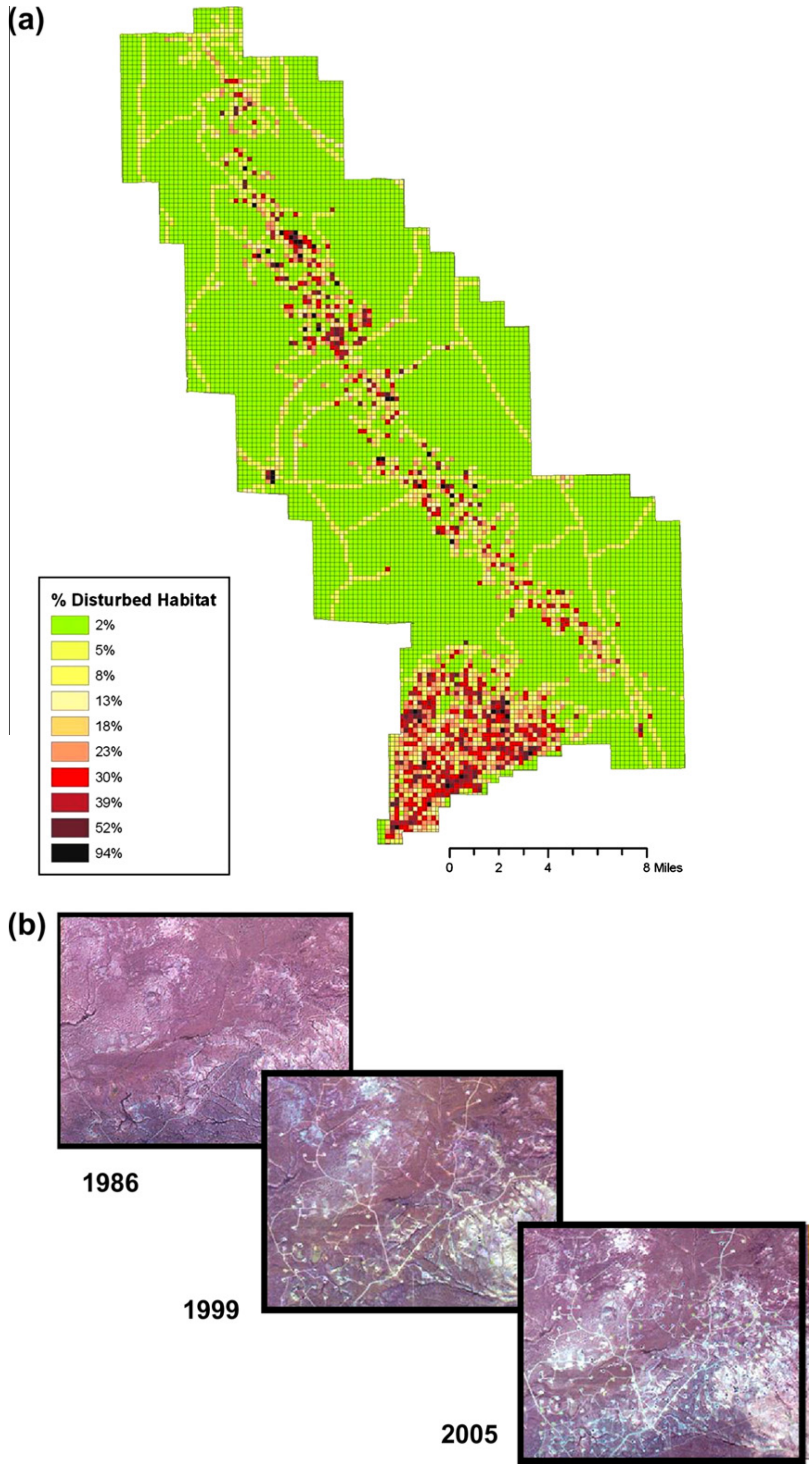

Fig. 4. (a) A 300 m × 300 m polygon grid was used to standardize our analysis of habitat loss. Total proportion of surface disturbance from construction of wells pads and roads was calculated for each cell. Data shown are for 2009 as an example. (b) Roads and well pads in one region of the Upper Green River Basin gas fields via satellite images from 1986 to 2005 showing habitat loss and fragmentation (images are of the same region of the UGRB, at the same spatial scale across each year and are used with permission from SkyTruth).

decisions about habitat selection at large spatial scales (see Kie et al., 2002). The total area within the hand-digitized road and well polygons was then summed and divided by the area of each grid cell (900 m^2) to determine the proportion of habitat disturbed within each 900 m^2 cell (see Fig. 4a as an example).

2.4. Snow depth modeling

We sampled snow depths each year with a 2-m probe at 81 fixed locations throughout the UGRB (see Beckmann et al., 2011 for snow depth survey locations) on a monthly basis during winter when snow was present. All measures were taken at least 10 m from the road in a randomized direction. The snow models were only applied in the RSF models (see below) within the PAPA and Jonah gas field boundaries. To model the patterns of variation given the uneven distribution of snow across the study area, we used an inverse distance weighted (IDW) technique, which determines cell values using a linear weighted combination of a set of sample points (Philip and Watson, 1982; Watson and Philip, 1985). We used the IDW tool from Arc Toolbox in ArcView 9.3 (Environmental Systems Research Institute, Redlands, CA) to interpolate snow depth. The output cell size and resolution grid was set to 30 m.

2.5. Habitat selection by pronghorn in gas fields

2.5.1. Habitat characteristics

We restricted the analysis to areas within the boundaries of the PAPA and Jonah Fields as these are the areas consistent with the extent of available GIS layers on habitat loss from development (Figs. 1 and 4). We identified nine habitat characteristics as potentially important factors influencing pronghorn distribution during winter: elevation, slope, aspect, distance to nearest road, distance to nearest well pad, well-pad status, habitat loss (labeled disturbance), vegetation, and snow depth. Vegetation was classified as sagebrush, irrigated crops, riparian, or a category labeled "other" that included desert shrub, mixed grasslands, and exposed rock/soil (Reiners et al., 1999). As a surrogate for human activity and traffic volume, well pads were classified based on their phase in the production cycles as: active (i.e., wells on which active drilling was occurring, wells that transitioned from drilling to production during the current winter, and wells in production prior to the start of the current winter), inactive (i.e., wells that were either abandoned or on which drilling did not begin until after March 31st of the current year), or unknown (i.e., generally cleared areas/structures that were visible on the satellite image but for which information was not available in the Wyoming Oil and Gas Conservation Commission database [http://wogcc.state.wy.us/] because they were infrastructure other than wells). We calculated slope and aspect from a 26-m digital elevation model using the Spatial Analyst extension in ArcInfo 9.3. We assigned grid cells with slopes $\geqslant 2^{\circ}$ to one of four aspect categories: northeast, southeast, southwest, or northwest. Grid cells with slopes $<2^{\circ}$ were classified as flat and included in the analysis as a reference category. We measured direct habitat loss as the proportion of disturbed habitat based on our grid cell analysis. We considered quadratic terms for elevation, snow depth, distance to nearest well pad, distance to nearest road, and slope to allow for non-linear relationships in pronghorn response. Following convention, a linear term for each variable was included along with the quadratic term (Zar, 1999). In addition, we tested interaction terms for distance to nearest well and snow depth, distance to nearest road and snow depth, disturbance (i.e., habitat loss) and snow depth, and well distance and well status, to allow pronghorn response to vary with increasing snow depth and increasing levels of human activity.

2.5.2. Mixed effects model development

We used mixed-effects resource selection function models (Zuur et al., 2009) to identify factors influencing habitat use by pronghorn. Mixed-effects models offer two important advantages over the traditional fixed-effects methods; random intercepts account for unbalanced sample designs (*e.g.*, the number of GPS locations differs among animals) and random intercepts and coefficients improve model fit given variation in selection among individuals and functional responses in selection (Gillies et al., 2006). In addition, mixed-effects models provide information on both population-level (represented by the fixed-effects) and individual-level (represented by the random effects) resource selection patterns (Hebblewhite and Merrill, 2008).

The analysis was performed separately for each year, which allowed for comparisons of factors influencing habitat selection both within and across years. Following Hebblewhite and Merrill (2008), we incorporated random effects into the traditional use-availability RSF design (Manly et al., 2002), in which covariates that may influence selection are compared at used and available locations. To measure resource availability, we generated a set of random points within the study area for each animal defined by boundaries of the PAPA and the Jonah (i.e., availability was assessed at the scale of the gas fields), with replacement, equivalent to the actual number of GPS locations recorded for the animal ($n_{\text{total}} = 48{,}622$ across all animals and all years; see number of GPS locations below for breakdown of number of random points each year). The random points were generated using the Hawth's Tools extension in ArcInfo 9.3 (Beyer, 2004). The random points were then randomly assigned to months in proportion to the actual GPS locations recorded for each animal. We measured the elevation, slope, aspect, vegetation, road distance, well distance, habitat loss, well status, and snow depth attributes associated with each random point using Hawth's Tools and Spatial Analyst in ArcInfo 9.3.

Random effects were incorporated in the RSF model (Manly et al., 2002) following Gillies et al. (2006), wherein resource covariates are compared at used and available locations using:

$$\hat{w}(x) = \exp(\mathbf{X\beta})$$

where $\hat{w}(x)$ is the relative probability of use as a function of covariates x_n, and $\mathbf{X\beta}$ is the vector of fixed-effects resource selection coefficients estimated from the fixed-effects logistic regression (Manly et al., 2002).

In addition to the fixed effects, we incorporated random effects in the RSF model to test for differences in selection among animals by including both a random intercept and random coefficients. Random effects were only considered for factors with four or more levels to avoid imprecise estimates (Bolker et al., 2008). Maximum-likelihood estimates were derived using generalized linear models with Laplace approximation (Bates and Maechler, 2009). To avoid including collinear variables which can produce unstable and misleading results, we screened all explanatory variables for correlation using a Spearman's pairwise correlation analysis with $r \geqslant 0.6$ as the threshold cut-off value. When the threshold was exceeded, only a single variable of the correlated pair was included in the model and alternate models were tested to identify the variable that best explained the data. Model-selection was performed by first identifying the covariates and interaction terms in the top-ranked fixed-effects model and then incorporating random effects to test for variation among individuals (Zuur et al., 2009). Akaike's Information Criterion (AIC) was used to rank models and evaluate model fit (Burnham and Anderson, 2002). We validated our models using area under the receiver operating characteristic curve (ROC) analyses. We used 10% of all GPS locations that were randomly pulled out each year prior to model development to assess validity of each year's model. All analyses were performed in R 2.9.1 using glm (R Development Core Team, 2009) or lmer in the lme4 package (Bates and Maechler, 2009).

Based on the population-level mixed-effects model, we mapped the predicted probability of use across the PAPA and Jonah Field using a 104 m × 104 m grid that covered the study area to be consistent with resource selection models for mule deer in the region (see Sawyer et al., 2006). Attributes associated with each grid cell were identified with the Spatial Analyst extension in ArcInfo 9.3. Predicted probability of use was estimated for each grid cell by applying the coefficients from the final population-level model using the raster calculator tool in Spatial Analyst. Grid cells (i.e., 104 m × 104 m) were assigned to one of four relative use categories (very high – 76–100%, high – 51–75%, medium – 26–50%, and low – 0–25%) based on quartiles of the distribution of predicted values.

3. Results

3.1. Habitat loss

Disturbance due to development in the gas fields has increased annually. In 2005, habitat loss due to construction of well pads was 9.9 km^2 in the PAPA and 11.0 km^2 in the Jonah. In 2009, habitat loss due to construction of well pads in the PAPA and Jonah had increased to 12.7 km^2 and 14.8 km^2, respectively. Over this 5-year span, the total amount of habitat loss due to well pad construction in the PAPA increased by 28.7% and in the Jonah by 34.1%.

Habitat loss in the PAPA from 2005 to 2009 due to road construction increased from 6.6 km^2 to 7.6 km^2. From 2005 to 2009, habitat loss in the Jonah Field due to road construction increased from 1.9 km^2 to 2.5 km^2. Total length of road constructed in the PAPA over the years has increased from 455 km to 510 km in 2009. In the Jonah, total length of road constructed increased during 2005–2009 from 213 km to 258 km. Between 2005 and 2009, the total length of roads increased in the PAPA by 12.1% and the Jonah by 20.7%. In 2007–2008, more road length was added in the PAPA than for all other years combined.

3.2. Snow depth

Snow in the PAPA and Jonah was typically deepest in February (Fig. 5). Highest average monthly snow depths were measured in February 2005 (25.9 cm) and February 2008 (26.6 cm), but average snow depths dropped in March 2005 to 7.0 cm. The lowest average monthly snow depths were measured in 2007 when both the maximum average monthly snow depth (14.5 cm in January) as well as the February average snow depth (10.0 cm) for 2007 were lower than any other year.

3.3. Habitat selection by pronghorn in gas fields

Of the 125 adult, female pronghorn captured inside gas fields, 117 were used to construct our RSF models. The remaining 8 collars were not recovered. Sample sizes to construct our RSF models by year were as follows: 2004–2005 – 5319 GPS locations for 20 pronghorn collected between 2/26/05 and 3/31/05 (Fig. 6a); winter 2005–2006 – 8826 GPS locations for 18 pronghorn collected between 1/24/06 and 3/31/06 (Fig. 6b); winter 2006–2007 – 15,186 GPS locations for 30 pronghorn collected between 1/1/07 and 3/31/07 (Fig. 6c); winter 2007–2008 – 10,792 GPS locations for 25 pronghorn collected between 1/7/08 and 3/31/08 (Fig. 6d); winter 2008–2009 – 8499 GPS locations for 24 pronghorn collected between 2/3/09 and 3/31/09 (Fig. 6e).

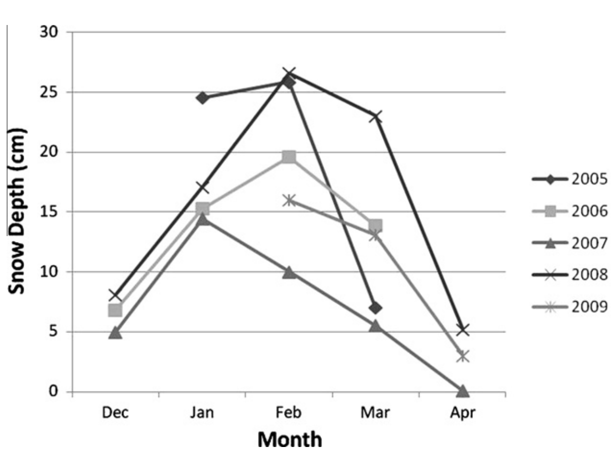

Fig. 5. Average monthly snow depths (cm) for each year (2005–2009) in the Upper Green River Basin of western Wyoming.

Among the habitat variables, there were high levels of correlation in all years between the slope and aspect variables ($r > 0.75$). Among the variables for gas-field development, there were high levels of correlation in all years between the variables for well-distance and road-distance ($r > 0.65$), and road-distance and habitat loss ($r > 0.70$). The variables for aspect, well-distance, and habitat loss (i.e., disturbance) produced models that better fit the data than those for slope or road-distance, so these three explanatory variables were retained in the final analysis.

Not surprisingly, pronghorn showed consistent selection across all winters for sagebrush areas relative to crops, riparian areas, and other types of vegetation. Irrigated crops were generally used more frequently than riparian areas in all years except the winters of 2006–2007 (when there was no significant difference) and 2007–2008. Relative to flat areas, pronghorn showed consistent selection for northeast, southeast, and southwest aspects. Habitat with a northwest aspect was used no differently than flat areas, or less frequently than flat areas, depending upon the year (Tables 1 and 2).

Across all winters, pronghorn consistently selected for habitat at lower elevation (Table 3). On average, habitat patches (i.e., 104 m × 104 m grid) with the highest probability of use were located 55 m lower than patches with the lowest probability of use (mean elevation = 2156 versus 2211 m). Pronghorn also consistently selected for habitat with less accumulated snow except in winter 2004–2005, which represented the highest snow year in the study (Table 3 and Fig. 5). These two factors appear to largely account for the reduced use by pronghorn of the northern and eastern portions of the gas fields, as elevation tends to decline along a north–south gradient, and snow depth along both a north–south and east–west gradient.

The impact of gas field development on pronghorn habitat use is determined by the interplay between a complex series of factors. Overall, probability of use declines as the distance to the nearest well pad increases, which is likely an indication that the most suitable winter habitat for pronghorn tends to be located above richer pockets of natural gas, which is clustered in the Jonah and along the spine of the Anticline (Figs. 4 and 6). Patches (i.e., 104 m × 104 m) with the highest probability of use were located an average of 504 m from the nearest gas well, versus 2777 m for patches with the lowest probability of use (Table 3). Within these preferred areas, the probability of use declines with increasing levels of habitat loss resulting from surface disturbance (Fig. 4 and Tables 1 and 2), which can likely be attributed to the lack of available forage since distance to nearest well and well status do not show conclusive associations. On average, habitat patches (i.e., 104 m × 104 m grid) with the highest probability of use have 3.8% surface disturbance due to construction of roads and well-pads versus 5.3% and 5.2% surface disturbance for patches with high to medium use, respectively (Table 3).

Among the three well-status classifications (active, inactive, unknown), there were no clear patterns of influence on habitat selection preferences. Although at least one of the well-status variables was significant in all years, the directionality of coefficients (positive or negative) varied annually, and the overall impact on the model was negligible (Tables 1 and 2). Thus, it appears that either: (1) human activity associated with different well-types has little impact on pronghorn habitat selection; (2) the well-status classifications did a poor job of characterizing fine-scale human activity levels associated with different well-types; or (3) the close proximity of various

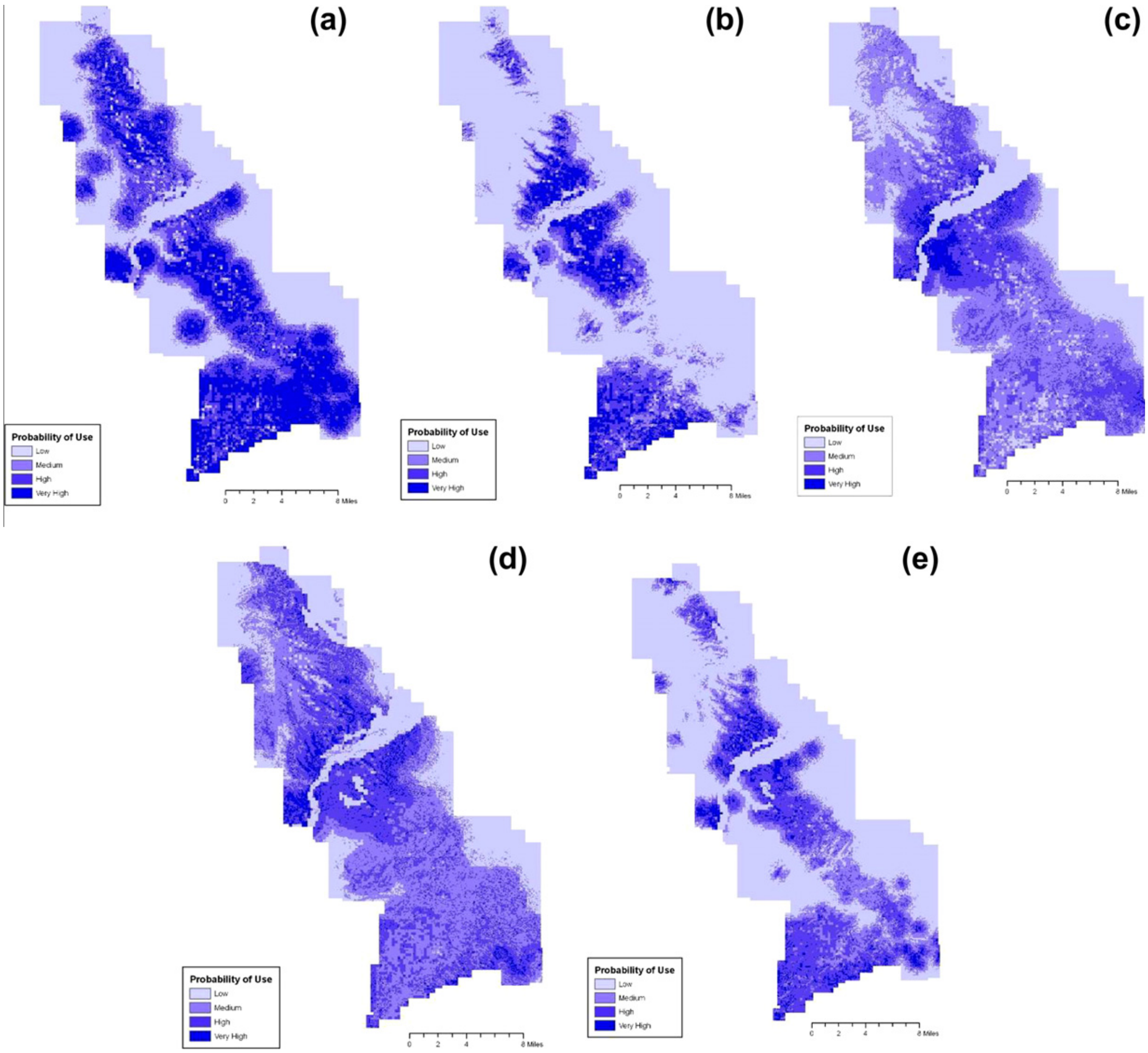

Fig. 6. Predicted probabilities and associated categories of pronghorn use of winter habitat as determined by mixed-effects resource selection function models in the Pinedale Anticline Project Area (PAPA) and Jonah gas fields in the Upper Green River Basin, Wyoming during the winters of (a) 2004–2005; (b) 2005–2006; (c) 2006–2007; (d) 2007–2008; and (e) 2008–2009. Darker shades correspond to higher predicted probabilities of use.

types of gas-field infrastructure with differing activity levels means that the status of the nearest well is not indicative of human activity levels at a coarser scale at which pronghorn may respond.

Similarly, there were no clear patterns of influence among the interaction terms between snow depth and well distance, snow depth and disturbance, or well distance and well status. The exception was the interaction between well distance and unknown wells which was negative (i.e., the probability of habitat use declined more rapidly with increasing distance from wells of unknown status compared to active wells) in the 4 years that the term was significant in the final model (Tables 1 and 2). In some years, pronghorn were more likely to use disturbed areas as snow depth increased (*e.g.*, 2007 and 2008), whereas in other years the use of disturbed areas declined with increasing snow depth (*e.g.*, 2005; Tables 1 and 2). As snow depth increased, the probability of use declined with increasing distance from the nearest gas well in 2005, 2006, and 2009, but increased with increasing distance to the nearest well in 2007, which represented the lowest snow year in the study (Tables 1 and 2 and Fig. 5). These results likely demonstrate the complex interactions and resulting interpretations between snow depth and gas field infrastructure on historic, pronghorn crucial winter range.

Nevertheless, there has been a 5-fold decline over the course of the study in the percentage of patches (i.e., 104 m × 104 m grid) classified as having a very high probability of use (from 28% in 2005 to 5% in 2009), and an increase in the percentage of patches classified as having a low probability of use (from 34% in 2005 to 53% in 2009; Fig. 7 and Table 3). These results indicate a general decline in the availability of high-quality habitat for pronghorn due to habitat alteration associated with gas field development (Figs. 6 and 7). In the absence of gas field development (i.e., we removed variables associated with gas field development), our 2009 model predicted that 17% of habitat patches (i.e., 104 m × 104 m grid) would be classified as having a very high probability of use, 46% as a high probability of use, 29% as a medium probability of use, and just 8% as a low probability of use as compared to the metrics calculated which include gas field development (Table 3).

The inclusion of random effects, which allow for variation in selection among individuals, resulted in a marked increase in model performance (Table 4). Although models that included a random intercept by animal performed only marginally better than the top-ranked fixed-effects models, the incorporation of random effects for distance to nearest well or habitat loss resulted in dramatic improvements in model fit, with the random coefficient for well-

Table 1
Parameter estimates for population-level resource selection function for pronghorn during three winters.

Parameter	2004–2005		2005–2006		2006–2007	
	β	*P*	*β*	*P*	*β*	*P*
Intercept	−213.492	<0.001	−1107.129	<0.001	283.250	<0.001
Vegetation-other		ns	−0.692	0.05	2.986	<0.001
Riparian	−1.065	0.001	−1.731	<0.001		ns
Sagebrush	1.879	<0.001	1.249	<0.001	3.428	<0.001
Well distance		ns	−1.144	0.01	0.291	0.10
Well distance^2	−0.422	<0.001		ns	−0.292	<0.001
Disturbance	−1.730	<0.001	−5.637	<0.001	−4.765	<0.001
NE aspect	1.001	<0.001		ns	0.506	<0.001
SE aspect	1.166	<0.001	1.225	<0.001	0.688	<0.001
SW aspect	0.791	<0.001	0.888	<0.001	0.285	<0.001
NW aspect		ns	−0.819	<0.001	−0.305	<0.001
Elevation	1979.599	<0.001	10373.946	<0.001	−2521.148	<0.001
Elevation^2	−4619.821	<0.001	−24320.571	<0.001	5535.838	<0.001
Snow depth	−13.552	<0.001	32.681	<0.001		ns
Snowdepth^2	67.640	<0.001	−133.536	<0.001	−18.824	<0.001
Inactive well		ns	−0.679	<0.001	0.093	0.05
Unknown well	0.600	<0.001	−0.183	0.05	−0.499	<0.001
Well distance:inactive well		ns	−0.143	0.05	0.057	0.10
Well distance:unknown well	−0.646	<0.001	−0.424	<0.001		ns
Well distance:snow depth	−2.308	<0.001	−3.530	<0.001	1.561	<0.001
Disturbance:snow depth	−22.467	<0.001		ns	6.273	0.10

Table 2
Parameter estimates for population-level resource selection function for pronghorn during the winters of 2007–2008 and 2008–2009.

Parameter	2007–2008		2008–2009	
	β	*P*	*β*	*P*
Intercept	14.962	<0.001	−351.316	<0.001
Vegetation-other		ns		ns
Riparian	1.092	<0.001	−1.287	<0.001
Sagebrush	3.583	<0.001	2.286	<0.001
Well distance		ns	−1.597	0.01
Well distance^2	−0.154	<0.001		ns
Disturbance	−5.280	<0.001	−4.180	<0.001
NE aspect	1.004	<0.001	0.733	<0.001
SE aspect	0.937	<0.001	0.807	<0.001
SW aspect	0.616	<0.001	0.561	<0.001
NW aspect		ns	−0.752	<0.001
Elevation	−85.766	<0.001	3347.365	<0.001
Elevation^2		ns	−7991.814	<0.001
Snow depth	8.545	<0.001		ns
Snow depth^2	−40.719	<0.001		ns
Inactive well	−0.229	<0.001	0.080	ns
Unknown well	0.327	<0.001	0.558	<0.001
Well Distance:inactive well	0.102	0.01		ns
Well Distance:unknown well	−0.263	<0.001	−0.382	<0.001
Well distance:snow depth		ns	−1.663	<0.001
Disturbance:snow depth	21.311	<0.001		ns

distance out-performing the coefficient for habitat loss in all years, accounting for more of the variation in the data (Table 4). The five final models had area under the receiver operating characteristic curve (ROC) values ranging from 0.82 to 0.90 ($AUC_{2005} = 0.86$, $AUC_{2006} = 0.82$, $AUC_{2007} = 0.89$, $AUC_{2008} = 0.86$, $AUC_{2009} = 0.90$) using the independent validity test data, indicating useful and accurate models (Swets, 1988).

4. Discussion and conclusions

True impacts of increasing infrastructure, habitat loss, and fragmentation to extract natural resources may be masked or dampened for populations held below a region's ecological food ceiling by hunting. However, if populations maintained below a food ceiling respond to habitat loss and fragmentation, then we can infer impacts from development for resource extraction can be substantial. When impacts from natural resource extraction on such populations are masked or delayed, then threshold levels may be crossed before negative impacts are identified and too late for appropriate adaptive management responses to be initiated in a timely manner. Determining if behavioral impacts are realized by wildlife populations prior to demographic responses to a sequentially increasing human-footprint from natural resource extraction would allow those concerned with conserving or managing wildlife the ability to identify impacts before thresholds of demographic responses are crossed. Alternatively, behavioral shifts in resource selection and habitat use in response to human activity or habitat loss may reduce or preclude long term demographic impacts, an issue that awaits further investigation in developing gas fields.

In the case of pronghorn of the Upper Green River Basin, we demonstrated significant changes in behavioral responses and resource selection patterns at both the population and individual-level during a relatively short 5-year period. These shifts due to energy development were detected despite the fact that this population is held below the food ceiling of the region due to high human harvest. On average, more than 2450 pronghorn/year are removed from the six hunt units in our 4000 km^2 study site (Wyoming Game and Fish, unpub. data). Nevertheless, shifts in pronghorn resource selection in relation to a sequentially increasing industry footprint in the UGRB were detectable. Behavioral responses by species to habitat loss may be a precursor to population impacts, such as lower reproduction and survival rates in subsequent years in regions rapidly and sequentially increasing in natural resource extraction infrastructure. The ability to detect behavioral responses prior to demographic responses would allow land and wildlife management agencies to appropriately adjust both spatial and temporal parameters of development to avoid potential demographic effects. The competing hypothesis is that shifts in behavior may preclude any demographic responses to development.

Our data reveal that by focusing on habitat use and behavioral shifts, we detected fine-scale avoidance of patches with high levels of disturbance. Notably, this included an 82% decline in the number of patches classified as highest quality. Such behavioral impacts may serve as a caution to pending negative demographic impacts in this population as the human-footprint grows in the UGRB.

Table 3
Average metrics associated with habitat patches (i.e., 104 m × 104 m grid) based on relative probability of use by pronghorn during the winters of 2004–2005 through 2008–2009.

Use category	Patches %	Elevation (m)	Habitat loss (%)	Snow (cm)	Well distance (m)
2008–2009					
Low	53	2210	1.40	17	2252
Medium	19	2199	5.70	15.3	565
High	23	2173	9.50	14.9	274
Very high	5	2155	7.90	14.2	206
2007–2008					
Low	18	2213	2.20	15.6	3556
Medium	40	2210	5.80	15.1	1142
High	36	2179	3.60	14.7	783
Very high	5	2154	2.60	14	657
2006–2007					
Low	28	2218	5.45	15.4	2809
Medium	42	2208	4.13	12.5	1056
High	26	2168	1.51	10.1	890
Very high	4	2121	0.88	8.5	917
2005–2006					
Low	62	2212	1.80	18.7	2139
Medium	13	2183	5.60	15	772
High	14	2171	7.40	13.4	429
Very high	11	2158	4.90	12.4	288
2004–2005					
Low	34	2200	1.61	26	3129
Medium	14	2201	4.95	25.4	1188
High	24	2197	4.52	26.2	692
Very high	28	2190	2.95	28.3	452

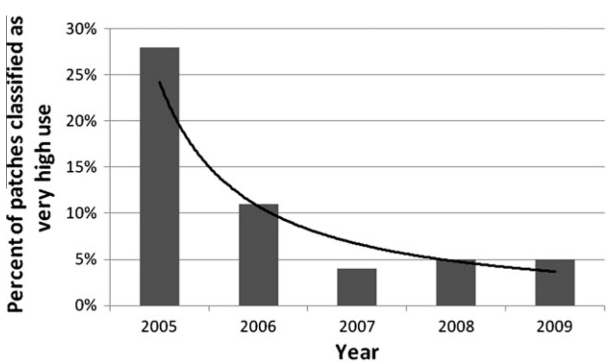

Fig. 7. Percent of patches classified as very high use for pronghorn in winter in the PAPA and Jonah gas fields in the Upper Green River Basin, Wyoming using mixed-effects resource selection function models developed from 125 GPS-collared adult female pronghorn from 2005 to 2009. Patches classified as very high use for pronghorn have declined by 82% over the 5-year period of 2005–2009. The line represents a line-of-best-fit.

The ability to detect behavioral impacts through avoidance at a fine spatial scale may be important even where demographic impacts are not the primary current. Further efforts will reveal if such nuanced behavior is an important precursor for understanding whether energy-related impacts will lead to population declines.

Ungulate winter resource selection is complicated, influenced by many factors, and varies among individuals, area, and conditions. Modeling these interactions requires a careful balance between accounting for influential factors and reducing variation in the models. In general, wintering pronghorn in the gas fields of the UGRB select for sagebrush dominated areas with shallow snow. The fact that pronghorn use of disturbed areas declined with increasing snow depths in the winter of 2005—a trend that was reversed in other years—may reflect the early peak (January and February) in snow depths in 2005 making adequate forage in disturbed areas inaccessible during the most critical months for energy retention. Across all winters except 2005, pronghorn utilized areas closer to gas wells when snow depths were greater, perhaps using associated roads to facilitate movement. In general, barring 2005, the interactive snow depth parameters suggest that when snow is deeper, pronghorn are more likely to use areas closer to disturbance and wells. This is likely because those disturbed areas are situated in the most crucial pronghorn winter habitat that becomes necessary during winters of high snowfall, especially in DA2 and DA3 in the PAPA. This spatial relationship is likely a result of the Anticline (uplift below the surface) that trapped the gas being located directly beneath the Mesa, the high plateau inside the PAPA that is wind swept during winter and which provides key crucial winter range for pronghorn and other ungulates in the region (Burke et al., 1989; BLM, 2006; Sawyer et al., 2006; Sawyer and Nielson, 2010). Pronghorn are likely constrained in their response to gas field infrastructure because it is being developed in areas that pronghorn have historically used as crucial winter range in the UGRB. In fact, the Wyoming Game and Fish Department has identified the Mesa region inside the PAPA natural gas field as crucial winter range for pronghorn for more than 50 years prior to gas field development.

Over time, our models demonstrate that gas field development is leading to a significant decrease in the number and amount of highest quality habitat patches (very high probability of use) and an increase in the number and amount of marginal/poor habitat patches (low probability of use). When we look at data from winter 2008–2009 without including natural gas development as variables in our models, the ratio of habitat patches that are predicted to be of highest quality are similar to the ratios predicted in both 2004–2005 and 2005–2006, when habitat disturbance across the gas fields was lower. In other words, when variables related to impacts of gas fields (*e.g.*, well pads, roads, distance to well pads, distance to roads, habitat loss) are removed from our resource selection models in 2009, the amount of high quality habitat on the landscape returns to 2004–2005 levels. This together with the fact that the parameter estimate for level of disturbance showed a consistent negative relationship with habitat use, demonstrates that habitat disturbance/loss appears to be the principal factor in determining pronghorn winter habitat use in the gas fields at both the individual- and population-level. Because this

Table 4
Comparison of top-ranked fixed-effects model with models containing a random intercept and random coefficient for well-distance and disturbance, 2005–2009.

Model structure	Variance		
	AIC	Intercept	Coefficient
2005			
Top-ranked fixed-effects model	11,767		
Top-ranked fixed-effects model with random intercept by animal	11,769	0.002	
Top-ranked fixed-effects model with random coefficient for well-distance by animal	11,202	0.580	0.777
Top-ranked fixed-effects model with random coefficient for disturbance by animal	11,716	0.017	10.207
2006			
Top-ranked fixed-effects model	15,961		
Top-ranked fixed-effects model with random intercept by animal	15,940	0.018	
Top-ranked fixed-effects model with random coefficient for well-distance by animal	15,019	0.674	3.224
Top-ranked fixed-effects model with random coefficient for disturbance by animal	15,580	0.195	56.916
2007			
Top-ranked fixed-effects model	36,293		
Top-ranked fixed-effects model with random intercept by animal	36,251	0.019	
Top-ranked fixed-effects model with random coefficient for well-distance by animal	34,167	0.737	0.811
Top-ranked fixed-effects model with random coefficient for disturbance by animal	35,692	0.054	79.615
2008			
Top-ranked fixed-effects model	26,071		
Top-ranked fixed-effects model with random intercept by animal	26,051	0.012	
Top-ranked fixed-effects model with random coefficient for well-distance by animal	24,582	0.629	3.053
Top-ranked fixed-effects model with random coefficient for disturbance by animal	25,314	0.094	50.481
2009			
Top-ranked fixed-effects model	19,531		
Top-ranked fixed-effects model with random intercept by animal	19,494	0.026	
Top-ranked fixed-effects model with random coefficient for well-distance by animal	17,974	0.873	7.97
Top-ranked fixed-effects model with random coefficient for disturbance by animal	18,776	0.262	68.208

is the case, over time as more habitat disturbance and loss has occurred due to gas field infrastructure, we have continued to see further shifts in pronghorn behavior and resource selection patterns resulting in a loss of high quality habitat patches due to behavioral avoidance of the areas most intensively developed in the gas fields.

In fact, patches of habitat which were predicted to be of very high use by pronghorn during winter inside the PAPA and Jonah gas fields have declined in abundance over the 5 year period from 2005 to 2009 by 82%. This trend indicates a fivefold loss in percentage of very high use patches (i.e., 104 m $\times$ 104 m) and represents a significant loss of high value winter habitat for pronghorn in the PAPA and Jonah gas fields over a very short period of time due to gas field development and infrastructure. There was a precipitous decline (61%) in the amount of highest quality habitat patches (very high probability of use patches; 104 m $\times$ 104 m grid) from year one (winter 2004–2005) to year two (winter 2005–2006), followed by a leveling off in the decline in subsequent years (Fig. 7). However, between year two (winter 2005–2006) and year three (winter 2006–2007) there was an additional loss of half (10% down to 5%) of the remaining habitat patches (i.e., 104 m $\times$ 104 m grid) classified as highest quality. In total, between the second and fifth years of our study there was an additional 20% loss of highest quality habitat patches following the precipitous 61% loss in the first year suggesting a sequential loss of high quality habitat over the course of our 5-year study.

It could be argued that this leveling off in the rate of decline is more representative of annual variation rather than further decline. Pronghorn are tolerant of some level of human activity and behavioral modifications to human activity may preclude future demographic impacts. However, there is the possibility that pronghorn responses to gas field development may lead to declines in highest quality habitat patches in a manner reflecting thresholds, where the decline takes the form of steps and at this time the first big step was shown from 2005 to 2007. This is an idea that warrants further investigation as these gas fields develop.

Wildlife populations can only withstand a certain level of loss of crucial wintering habitat and resulting shifts in behavior, locations, and use before demographic impacts are realized. Here we demonstrated that the ability to detect behavioral impacts before demographic impacts suggests that at least for some species, behavior may be a better sentinel and earlier warning for negative impacts of natural resource extraction on wildlife populations than studies focused solely on demography. Nevertheless, disentangling cause and effect through the use of behavior and resource selection patterns will be an important consideration.

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CHAPTER 14

Petroleum and Individual Polycyclic Aromatic Hydrocarbons

Peter H. Albers

CONTENTS

14.1 INTRODUCTION

Crude petroleum, refined petroleum products, and individual polycyclic aromatic hydrocarbons (PAHs) contained within petroleum are found throughout the world. Their presence has been detected in living and nonliving components of ecosystems. Petroleum can be an environmental hazard for all organisms. Individual PAHs can be toxic to organisms, but they are most commonly associated with illnesses in humans. Because petroleum is a major environmental source of these PAHs, petroleum and PAHs are jointly presented in this chapter. Composition, sources, environmental fate, and toxic effects on all organisms of aquatic and terrestrial environments are addressed.

Petroleum spills raised some environmental concern during the early twentieth century when ocean transport of large volumes of crude oil began.[1] World War I caused a large number of oil spills that had a noticeably adverse effect on marine birds. The subsequent conversion of the economy of the world from coal to oil, followed by World War II, greatly increased the petroleum threat to marine life. Efforts to deal with a growing number of oil spills and intentional oil discharges at sea continued during the 1950s and 1960s.[1] The wreck of the *Torrey Canyon* off the coast of England in 1967 produced worldwide concern about the consequences of massive oil spills in the marine environment. Research on the environmental fate and biological effects of spilled petroleum increased dramatically during the 1970s. The *Exxon Valdez* oil spill in Prince William Sound, Alaska, in 1989, and the massive releases of crude oil into the Arabian Gulf during the 1991 Gulf War again captured international attention and resulted in an increase in environmental research. Despite considerable progress in developing methods to clean up spills, the adoption of numerous national and international controls on shipping practices, and high public concern (e.g., passage of the Oil Pollution Act of 1990 [33 USCA Sec. 2701-2761] in the United States), petroleum continues to be a widespread environmental hazard.

The association between skin cancer in chimney sweeps and exposure to contaminants in soot was made in England during the late eighteenth century. By the early twentieth century, soot, coal tar, and pitch were all known to be carcinogenic to humans. In 1918 benzo(a)pyrene was identified as a major carcinogenic agent; other PAHs have since been identified as carcinogenic or tumorigenic. Many toxic and carcinogenic effects of PAHs on humans, laboratory animals, and wildlife have been described in numerous reviews.[2]

14.2 COMPOSITION AND CHARACTERISTICS

14.2.1 Petroleum

Petroleum consists of crude oils and a wide variety of refined oil products. Crude oils vary in chemical composition, color, viscosity, specific gravity, and other physical properties. Color ranges from light yellow-brown to black. Viscosity varies from free flowing to a substance that will barely pour. Specific gravity of most crude oils varies between 0.73 and 0.95.[3] Refined oil products most often spilled in large quantities are aviation fuel, gasoline, No. 2 fuel oil (diesel fuel), and No. 6 fuel oil (bunker C). Fuel oils (Nos. 1 to 6) become increasingly dense and viscous and contain increasingly fewer volatile compounds as their numeric classification proceeds from one to six.

Crude oil is a complex mixture of thousands of hydrocarbon and nonhydrocarbon compounds. Hydrocarbons comprise more than 75% of most crude and refined oils; heavy crude oils can contain more than 50% nonhydrocarbons.[3,4] Hydrocarbons in petroleum are divided into four major classes: (1) straight-chain alkanes (n-alkanes or n-paraffins), (2) branched alkanes (isoalkanes or isoparaffins), (3) cycloalkanes (cycloparaffins), and (4) aromatics (Figure 14.1). Alkenes occur in crude oil, but they are rare. A variety of combinations of the different types of compounds occur. Low-molecular-weight members of each class predominate in crude oils. Aliphatic hydro-

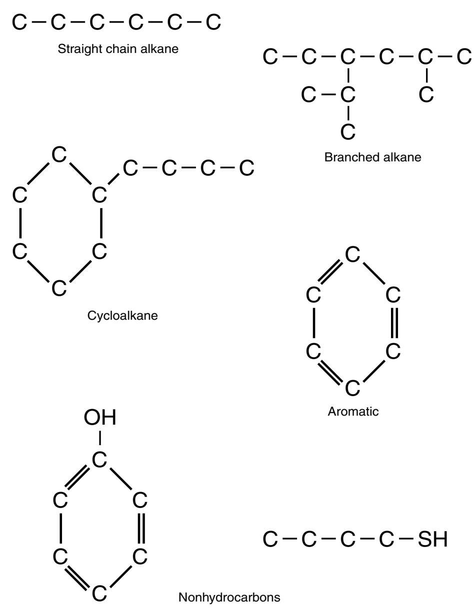

Figure 14.1 Types of molecular structures found in petroleum.[3] Hydrogen atoms bonded to carbon atoms are omitted.

carbons have the carbon atoms arranged in an open chain (straight or branched). Aromatic hydrocarbons have the carbon atoms arranged in ring structures (up to six), with each ring containing six carbon atoms with alternating single and double bonds. The aliphatic hydrocarbons (except alkenes) have maximum hydrogen content (saturated), whereas the aromatic hydrocarbons do not have maximum hydrogen content (unsaturated) because of the alternating double bonding between carbon atoms. Nonhydrocarbons in petroleum are compounds containing oxygen (O), sulfur (S), nitrogen (N) (Figures 14.1 and 14.3), or metals, in addition to hydrogen and carbon, and can range from simple open-chain molecules to molecules containing 10 to 20 fused aromatic and cycloalkane carbon rings with aliphatic side chains. The largest and most complex nonhydrocarbons are the resins and asphaltenes.

Crude oils are classified according to physical properties or chemical composition.[3,5] Specific gravity determines whether oil is classified as light, medium, or heavy. Crude oils also can be partitioned into chemical fractions according to boiling point. The relative amounts of compounds in various categories are sometimes used to classify oil (e.g., paraffinic, napthenic, high or low sulfur).

14.2.2 PAHs

Polycyclic aromatic hydrocarbons are aromatic hydrocarbons with two or more fused carbon rings that have hydrogen or an alkyl (Cn H2n+1) group attached to each carbon. Compounds range from naphthalene (C10 H8, two rings) to coronene (C24 H12, seven rings) (Figure 14.2). Crude oils contain 0.2 to 7% PAHs, with configurations ranging from two to six rings; PAH content increases with the specific gravity of the oil.[6–8] In general, PAHs have low solubility in water, high melting and boiling points, and low vapor pressure. Solubility decreases, melting and boiling points increase, and vapor pressure decreases with increasing molecular volume. Investigators assessing biological effects sometimes group true PAHs with compounds consisting of aromatic and nonaromatic rings, or compounds with N, S, or O within the ring (heterocycle) or substituted for attached hydrogen (Figure 14.3).

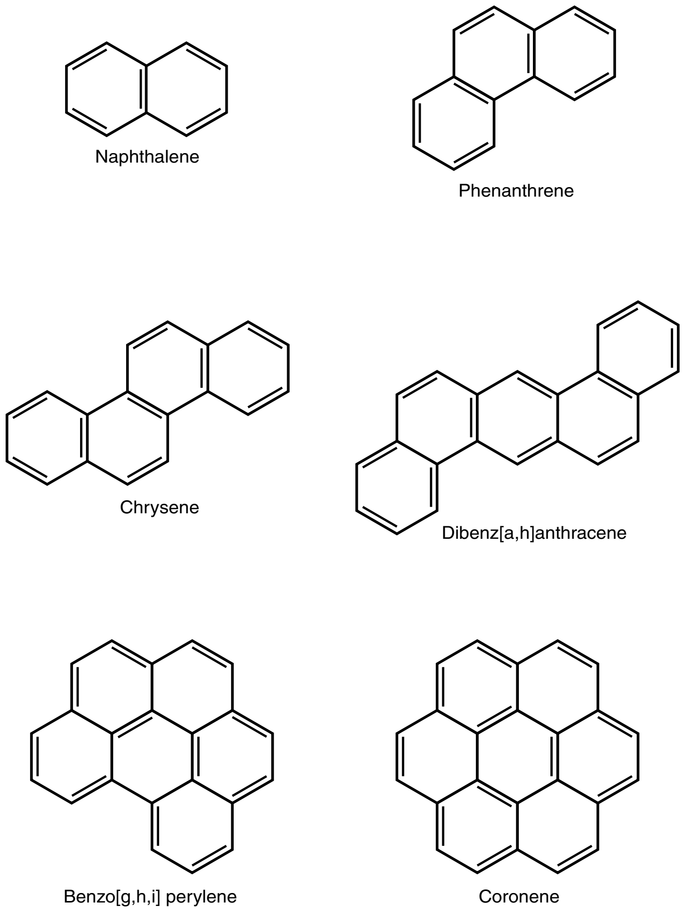

Figure 14.2 Examples of PAH compounds without attached alkyl groups.[16] Hydrogen atoms bonded to carbon atoms are omitted.

14.3 SOURCES

14.3.1 Petroleum

During the early 1970s about 35% of the petroleum hydrocarbons in the marine environment came from spills and discharges related to marine transportation; the remainder came from offshore oil and gas production, industrial and municipal discharges, stormwater discharges, river runoff, atmospheric deposition, and natural seeps[9,10] (Figure 14.4). Transportation spills and discharges probably accounted for less than 35% of the total oil discharged onto land and freshwater environments.[10] Estimates for the late 1970s indicated that about 45% of the petroleum hydrocarbons in the marine environment came from spills and discharges related to marine transportation.[11] In heavily used urban estuaries, the contribution of transportation spills and discharges to total petroleum hydrocarbon input can be 10% or less.[12,13] By contrast, the largest source of petroleum in coastal or inland areas removed from urban or industrial centers is petroleum transportation. In the 1980s and 1990s, war, terrorism, vandalism, and theft became additional, and sometimes major, causes of petroleum discharges into water and land environments.[14,15]

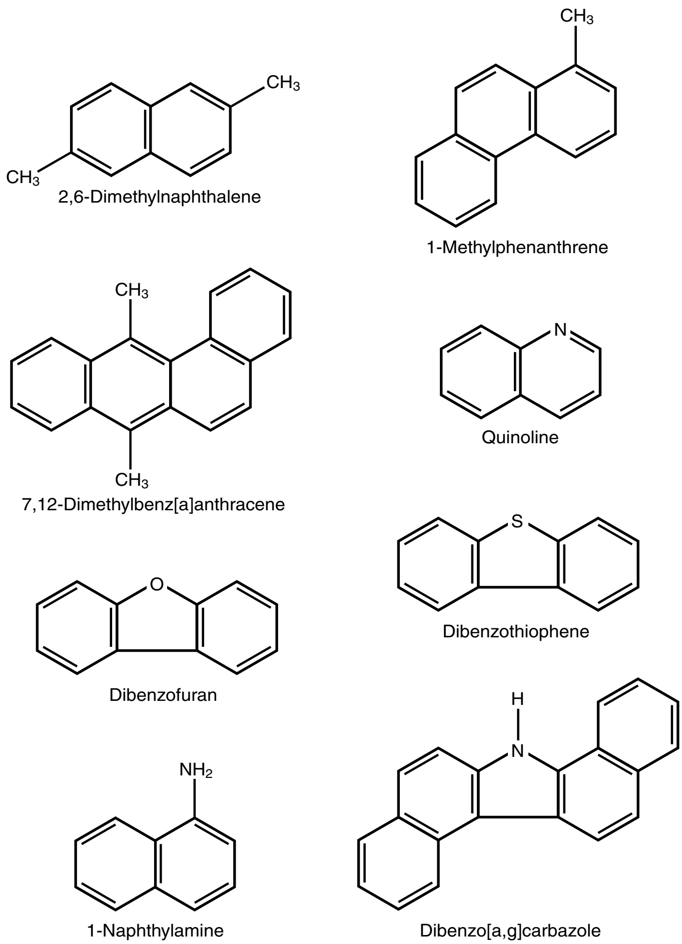

Figure 14.3 Examples of PAH compounds with attached alkyl groups and aromatic compounds with nitrogen, sulfur, or oxygen.[8] Except for the alkyl groups, hydrogen atoms bonded to carbon atoms are omitted.

14.3.2 PAHs

Most PAHs are formed by a process of thermal decomposition (pyrolysis) and subsequent recombination (pyrosynthesis) of organic molecules.[16] Incomplete combustion of organic matter produces PAHs in a high-temperature (500 to 800°C) environment. All forms of combustion, except flammable gases well mixed with air, produce some PAHs. Subjection of organic material in sediments to a low-temperature (100 to 300°C) environment for long periods of time produces PAHs as coal and oil deposits within sedimentary rock formations (a.k.a. diagenesis).[7,17] Although the PAH compounds formed by high- and low-temperature processes are similar, the occurrence of alkylated PAHs is greater in the low-temperature process.[14] Biological formation of PAHs occurs in chlorophyllous plants, fungi, and bacteria.[2,8]

Natural sources of PAHs include forest and grass fires, oil seeps, volcanoes, plants, fungi, and bacteria. Anthropogenic sources of PAHs include petroleum, electric power generation, refuse incineration, and home heating; production of coke, carbon black, coal tar, and asphalt; and internal combustion engines.[2,7] The primary mechanism for atmospheric contamination by PAHs is incom-

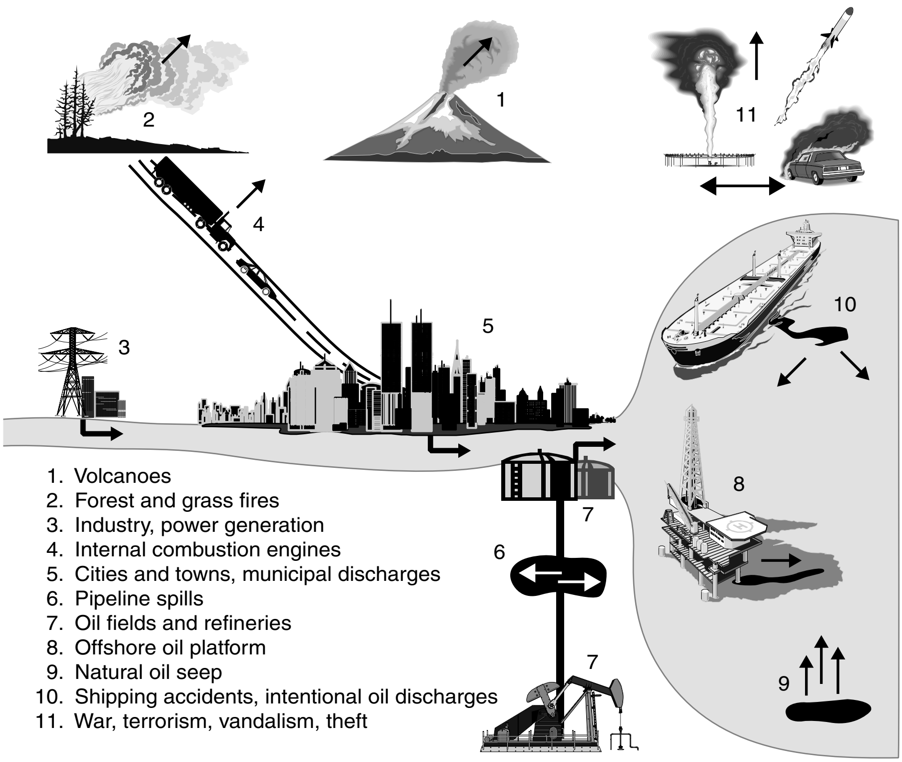

Figure 14.4 Sources of petroleum and PAHs in the environment. Arrows indicate the initial movement of PAH and petroleum into the air, water, and soil.

plete combustion of organic matter from previously mentioned sources.[15] Aquatic contamination by PAHs is caused by petroleum spills, discharges, and seepages; industrial and municipal wastewater; urban and suburban surface runoff; and atmospheric deposition.[2] Land contamination by PAHs is caused by petroleum spills and discharges, forest and grass fires, volcanoes, industrial and municipal solid waste, and atmospheric deposition.

14.4 ENVIRONMENTAL FATE

14.4.1 General Considerations

Petroleum is monitored as a liquid composed of a diverse array of thousands of compounds, but PAHs are monitored as a group of individual compounds with similar molecular structures. Polycyclic aromatic hydrocarbons from low- or high-temperature pyrolysis and pyrosynthesis of organic molecules have similar fates in the environment. Whereas PAHs from crude and refined oils and coal originate from a concentrated hydrocarbon source, PAHs produced by high temperature (combustion or industrial processes) are dispersed in the air, scattered on the ground, or included as a component of liquid waste and municipal sewage discharges.

14.4.2 Physical and Chemical

Petroleum discharged on water spreads quickly to cover large areas with a layer of oil varying from micrometers to centimeters thick. Some oils, especially heavy crudes and refined products,

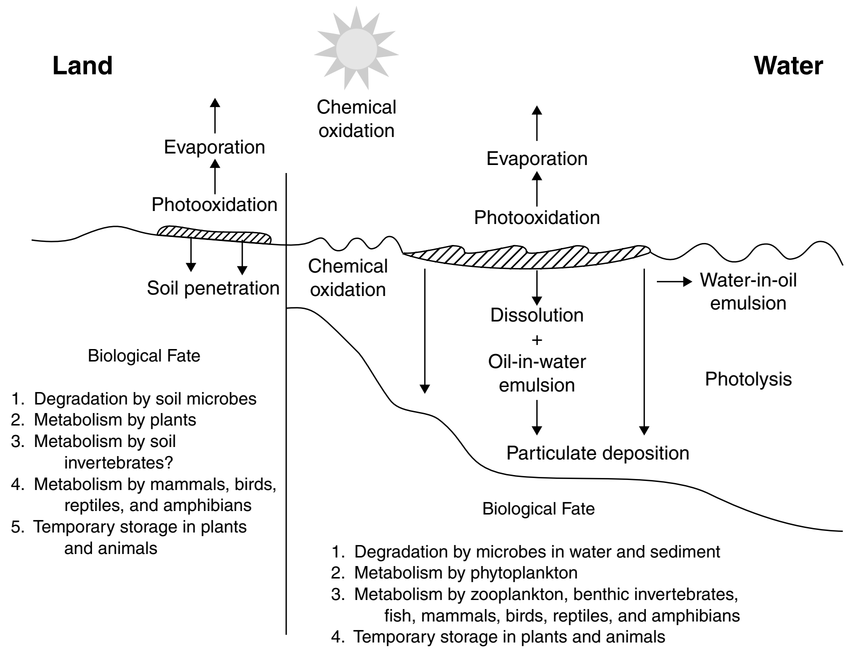

Figure 14.5 Chemical and biological fate of petroleum and PAHs in water and on land.

sink and move below the surface or along the bottom of the water body. Wave action and water currents mix the oil and water and produce either an oil-in-water emulsion or a water-in-oil emulsion. The former increasingly disperses with time, but the latter resists dispersion. Water-in-oil emulsions have 10 to 80% water content; 50 to 80% of emulsions are often described as "chocolate mousse" because of the thick, viscous, brown appearance. Oil remaining on the water eventually forms tar balls or pancake-shaped patches of surface oil that drift ashore or break up into small pieces and sink to the bottom.

Polycyclic aromatic hydrocarbons released into the atmosphere have a strong affinity for airborne organic particles and can be moved great distances by air currents. The molecules are eventually transported to earth as wet or dry particulate deposition.[18]

Crude and refined oil products begin to change composition on exposure to air, water, or sunlight[3] (Figure 14.5). Low-molecular-weight components evaporate readily; the amount of evaporation varies from about 10% of the spilled oil for heavy crudes and refined products (No. 6 fuel oil) to as much as 75% for light crudes and refined products (No. 2 fuel oil, gasoline). Less than 5% of a crude oil or refined product (primarily low-molecular-weight aromatics and polar nonhydrocarbons) dissolves in water. Hydrocarbons exposed to sunlight, in air or water, can be converted to polar oxidized compounds (photooxidation). Degradation of hydrocarbons in water by photolysis occurs when oxygen is insufficient for photooxidation; high-molecular-weight aromatic hydrocarbons are particularly likely to be altered by this mechanism.[7] Chemical oxidation of aromatic hydrocarbons can result from water and wastewater treatment operations[7] and chemical reactions in the atmosphere.[18]

14.4.3 Biological

The movement of oil from the water surface into the water column by dissolution and emulsion exposes the molecules and particles of oil to degradation and transport by organisms. Microbes (bacteria, yeast, filamentous fungi) in the water metabolize the light and structurally simple hydrocarbons and nonhydrocarbons.[3,19] Heavy and complex compounds are more resistant to microbial degradation and eventually move into bottom sediments. Oil particles and individual hydrocarbons (petroleum or recent pyrosynthesis) also adhere to particles (detritus, clay, microbes, phytoplankton) in the water and settle to the bottom, where a variety of microbes metabolize the light and structurally simple compounds. About 40 to 80% of a crude oil can be degraded by microbial action.[3]

Oil and anthropogenic PAHs are ingested by a variety of invertebrate and vertebrate organisms, in addition to microbes. Mammals, birds, fish, and many invertebrates (crustaceans, polychaetes, echinoderms, insects) metabolize and excrete some of the hydrocarbons ingested during feeding, grooming, and respiration.[2,20–24] Although bivalve mollusks and some zooplankton are either unable or marginally able to metabolize oil, they can transport and temporarily store it. Terrestrial plants and aquatic algae can assimilate and metabolize hydrocarbons.[2,25,26] Some soil invertebrates could be capable of metabolizing oil and anthropogenic PAHs, but evidence is absent from the literature.

Accumulation of hydrocarbons is usually inversely related to the ability of the organism to metabolize hydrocarbons.[2,6] For example, bivalve mollusks have a poorly developed mixed function oxygenase (MFO) capability and accumulate hydrocarbons rapidly. After acute exposure, depuration of light for structurally simple hydrocarbons, especially aliphatic hydrocarbons, is more rapid than for heavy hydrocarbons, especially aromatic hydrocarbons.[2,8,27,28] Hydrocarbons accumulated by bivalves through chronic exposure are depurated slowly.[8,29] Organisms, such as fish and some crustaceans, that possess a well-developed MFO system (microsomal monooxygenases) are capable of metabolizing hydrocarbons and only accumulate hydrocarbons in heavily polluted areas.[2] Aquatic environmental factors that reduce the potential for hydrocarbon uptake and retention include high levels of dissolved or suspended organic material and warm water temperatures. Increases in PAH accumulation have not been observed in the trophic levels of aquatic ecosystems.[8,30] Aquatic and terrestrial mammals, birds, reptiles, and amphibians have well-developed MFO systems, but enzyme induction by hydrocarbons in these species is not as well described as in fish and some aquatic invertebrates.[31] Phytoplankton can accumulate aromatic hydrocarbons from water.[2] Terrestrial plants are poor accumulators of soil PAHs, presumably because PAHs strongly adsorb to soil organic material. Most of the PAHs detected in terrestrial plants appear to be derived from the atmosphere; PAHs adhere to or are absorbed by plant tissue. Following the death of vegetation, PAHs are deposited into the surface litter of soil.[2,27,32]

Organisms with high lipid content, a poor MFO system, and that exhibit activity patterns or distributions that coincide with the location of hydrocarbon pollution are most likely to accumulate hydrocarbons.[2,8] Once assimilated, heavy aromatic hydrocarbons (four or more benzene rings) are the most difficult group of hydrocarbons to excrete, regardless of MFO capability.[2,33]

14.4.4 Residence Time

Residence time for petroleum in water is usually less than 6 months. Residence time for petroleum deposited on nearshore sediments and intertidal substrate is determined by the characteristics of the sediment and substrate. Oil-retention times for coastal environments range from a few days for rock cliffs to as much as 20 years for cobble beaches, sheltered tidal flats, and wetlands.[34–38] Microbes in the sediment and on the shoreline metabolize petroleum compounds; microbial degradation is reduced considerably by anaerobic conditions.[39,40] In cold climates ice, low wave energy, and decreased chemical and biological activity cause oil to remain in sediments or on the shore longer than in temperate or tropical climates; sheltered tidal flats and wetlands can be expected to retain oil for long periods of time.[41,42] Total petroleum hydrocarbons or individual PAHs in undisturbed estuarine subtidal sediments can remain as identifiable deposits for many decades.[43]

Oil spilled on land has little time to change before it penetrates into the soil. Oil spilled on lakes and streams usually has less opportunity to change before drifting ashore than oil spilled on the ocean because the water bodies are smaller. Petroleum spilled directly on land is degraded by evaporation, photooxidation, and microbial action. Residence times for hydrocarbons in terrestrial soils are less well documented than for sediments but are determined by the same conditions (substrate type, oxygen availability, temperature, surface disruption) that determine residence times in intertidal sediments. Total petroleum hydrocarbons and individual PAHs can persist in soils of cold or temperate regions for at least 20 to 40 years; persistence of PAHs increases with increase in the number of benzene rings.[32,44–46]

14.4.5 Spill Response

Petroleum spills are sometimes left to disperse and degrade naturally,[47] but cleanup efforts are initiated when economically or biologically important areas are threatened. Oil-response actions include mechanical removal, chemical treatment, enhanced biodegradation, and restoration.[48,49] The addition of chemicals to floating oil for purposes of gelling, herding, or dispersing the oil can modify the expected effects of the oil. The chemicals themselves often have some toxicity, and in the case of dispersants, movement of oil into the water column is greatly accelerated. Enhanced biodegradation practices are evolving through experimentation, but the most common practice is the stimulation of indigenous microbial populations through application of supplemental nitrogen or phosphorus to oil on land or water. The addition of nitrogen and phosphorus to oiled shorelines in Prince William Sound, Alaska, accelerated biodegradation and did not increase toxicity or environmental effects of the oil.[50] The literature on oil-spill response procedures, cleanup methods, and restoration methods is extensive; the interested reader is encouraged to consult literature cited in references[47–50] and other sources for a more comprehensive treatment of this topic.

14.5 EFFECTS ON ORGANISMS

14.5.1 General

Petroleum can adversely affect organisms by physical action (smothering, reduced light), habitat modification (altered pH, decreased dissolved oxygen, decreased food availability), and toxic action. Large discharges of petroleum are most likely to produce notable effects from physical action and habitat modification. The aromatic fraction of petroleum is considered to be responsible for most of the toxic effects.

Polycyclic aromatic hydrocarbons affect organisms through toxic action. The mechanism of toxicity is reported to be interference with cellular membrane function and enzyme systems associated with the membrane.[7] Although unmetabolized PAHs can have toxic effects, a major concern in animals is the ability of the reactive metabolites, such as epoxides and dihydrodiols, of some PAHs to bind to cellular proteins and DNA. The resulting biochemical disruptions and cell damage lead to mutations, developmental malformations, tumors, and cancer.[2,6,51] Four-, five-, and six-ring PAHs have greater carcinogenic potential than the two-, three-, and seven-ring PAHs.[2,7] The addition of alkyl groups to the base PAH structure often produces carcinogenicity or enhances existing carcinogenic activity (e.g., 7,12-dimethylbenz[a]anthracene). Some halogenated PAHs are mutagenic without metabolic activation,[52] and the toxicity and possibly the carcinogenicity of PAHs can be increased by exposure to solar ultraviolet radiation.[53,54] Cancerous and precancerous neoplasms have been induced in aquatic organisms in laboratory studies, and cancerous and noncancerous neoplasms have been found in feral fish from heavily polluted sites.[2,7,55,56] However, sensitivity to PAH-induced carcinogenesis differs substantially among animals.[2,7]

In water the toxicity of individual PAHs to plants and animals increases as molecular weight (MW) increases up to MW 202 (fluoranthene, pyrene). Beyond MW 202 a rapid decline in solubility reduces PAH concentrations to less than lethal levels, regardless of their intrinsic toxicity. However, sublethal effects can result from exposure to these very low concentrations of high MW compounds.[7] Except for the vicinity of chemical or petroleum spills, environmental concentrations of PAHs in water are usually several orders of magnitude below levels that are acutely toxic to aquatic organisms. Sediment PAH concentrations can be much higher than water concentrations, but the limited bioavailability of these PAHs greatly reduces their toxic potential.[2] In general, caution should be employed when assessing the aquatic "toxicity" of biogenic or anthropogenic PAHs because bioavailability (solubility, sediment sequestration, mechanism of exposure) and chemical modification determine how much toxicity is realized.

14.5.2 Plants and Microbes

Reports of the effects of petroleum spills or discharges on plants and microbes contain accounts of injury or death to mangroves,[57,58] seagrasses,[59] and large intertidal algae;[60,61] severe and long-lasting (> 2 years) destruction of salt marsh vegetation[38,62–64] and freshwater wetland vegetation;[65,66] enhanced or reduced biomass and photosynthetic activity of phytoplankton communities;[67,68] genetic effects in mangroves and terrestrial plants;[69,70] and microbial community changes and increases in numbers of microbes (Table 14.1).[71–73] Differences in species sensitivity to petroleum are responsible for the wide variation in community response for phytoplankton and microbes.

Recovery from the effects of oil spills on most local populations of nonwoody plants can require from several weeks to 5 years, depending on the type of oil, circumstances of the spill, and species affected. Mechanical removal of petroleum in wetlands can markedly increase the recovery time.[74,75] Complete recovery by mangrove forests could require up to 20 years.[76] Phytoplankton and microbes in the water column of large bodies of water return to prespill conditions faster than phytoplankton and microbes in small bodies of water because of greater pollutant dilution and greater availability of colonizers in nearby waters.[77] Lethal and sublethal effects are caused by contact with oil or dissolved oil, systemic uptake of oil compounds, blockage of air exchange through surface pores, and possibly by chemical and physical alteration of soil and water, such as depletion of oxygen and nitrogen, pH change, and decreased light penetration.

The effects of petroleum on marine plants, such as mangroves, sea grasses, saltmarsh grasses, and micro- and macroalgae, and microbes have been studied with laboratory bioassays, experimental ecosystems, and field experiments and surveys (Table 14.1).[78–87] Petroleum caused death, reduced growth, and impaired reproduction in the large plants. Microalgae were either stimulated or inhibited, depending on the species and the type and amount of oil; response was expressed as changes in biomass, photosynthetic activity, and community structure. In response to petroleum exposure, community composition of indigenous bacteria was altered and total biomass increased.

The effects of petroleum on freshwater phytoplankton, periphyton, and microbes have been studied with laboratory bioassays and field experiments.[88–93] Petroleum induced effects similar to those described for marine microalgae and bacteria. Domestic and wild plants have been exposed to oiled soil in laboratory experiments[94–96] and tundra vegetation has been subjected to an experimental spill of crude oil.[97] Inhibition of seed germination, plant growth, and fungal colonization of roots was demonstrated in the laboratory bioassays. Death of herbaceous and woody plants and long-term community alteration were caused by the experimental tundra spill.

Individual PAHs, mostly two- and three-ring compounds, at low concentrations (5 to 100 ppb) can stimulate or inhibit growth and cell division in aquatic bacteria and algae. At high concentrations (0.2 to 10 ppm) the same PAHs interfere with cell division of bacteria and cell division and photosynthesis of algae and macrophytes; they can also cause death.[2,7]

Table 14.1 Effects of Petroleum or Individual PAHs on Organisms

Effect[a]	Type of Organism: Plant or Microbe	Invertebrate	Fish	Reptile or Amphibian	Bird	Mammal[b]
Individual Organisms						
Death	X	X	X	X	X	X
Impaired reproduction	X	X	X	X	X	X
Reduced growth and development	X	X	X	X	X	
Altered rate of photosynthesis	X					
Altered DNA	X	X	X	X	X	X
Malformations			X		X	
Tumors or lesions		X	X	X		X
Cancer			X	X		X
Impaired immune system			X		X	X
Altered endocrine function			X		X	
Altered behavior		X	X	X	X	X
Blood disorders		X	X	X	X	X
Liver and kidney disorders			X		X	X
Hypothermia					X	X
Inflammation of epithelial tissue				X	X	X
Altered respiration or heart rate		X	X	X		
Impaired salt gland function				X	X	
Gill hyperplasia			X			
Fin erosion			X			
Groups of Organisms[c]						
Local population change	X	X	X		X	X
Altered community structure	X	X	X		X	X
Biomass change	X	X	X			

[a] Some effects have been observed in the wild and in the laboratory, whereas others have only been induced in laboratory experiments or are population changes estimated from measures of reproduction and survival.
[b] Includes a sampling of literature involving laboratory and domestic animals.
[c] Populations of microalgae, microbes, soil invertebrates, and parasitic invertebrates can increase or decrease in the presence of petroleum, whereas populations of other plants and invertebrates and populations of vertebrates decrease.

14.5.3 Invertebrates

Reports of the effects of aquatic oil spills or discharges and oil-based drill cuttings often contain accounts of temporary debilitation, death, population change, or invertebrate community change for marine water column,[98,99] deepwater benthic,[100,101] nearshore subtidal,[102–105] intertidal,[64,106,107] coastal mangrove organisms,[102,108] and stream[109,110] and lake[111] organisms. For a review of the effects of petroleum on marine invertebrates, see Suchanek.[112] Observed effects are caused by smothering; contact by adults, juveniles, larvae, eggs, and sperm with whole or dissolved oil; ingestion of whole oil or individual compounds; and possibly by chemical changes in the water, including oxygen depletion and pH change. Accounts of the effects of petroleum spills or discharges on terrestrial invertebrates have not been published.

Recovery from the effects of oil spills on local populations of invertebrates can require as little as a week for pelagic zooplankton or as much as 10 years, or more, for nearshore subtidal meiofauna. Uncertainty of recovery time is particularly evident for intertidal, nearshore subtidal, and coastal mangrove biota; the prognosis for recovery is a function of the size of the spill, type of oil, season of year, weather, characteristics of affected habitat, and species affected. Chronic input of petroleum from natural seeps or anthropogenic sources produces communities of biota that are adapted to the hydrocarbon challenge; preexisting or continuing chronic input can complicate estimates of invertebrate recovery from ephemeral input. Aggressive cleaning of shorelines can retard recovery.[113] Zooplankton in large bodies of water return to prespill conditions faster than zooplankton in small bodies of water (isolated estuaries, lakes, stream headwaters) because of greater pollutant dilution and greater availability of colonizers in nearby waters.[77]

Much work has been done on the effects of petroleum on marine invertebrates with laboratory bioassays, mesocosms, enclosed ecosystems, and field experiments and surveys.[82,114–124] Less work has been conducted on freshwater invertebrates with laboratory bioassays and field experiments.[88,125–129] Among the effects reported are reduced survival, altered physiological function, soft-tissue abnormalities, inhibited reproduction, altered behavior, and changes in species populations and community composition.

Soil contaminated with petrochemicals has been associated with a reduced number of species and reduced species abundance of rodent parasites.[130] In contrast, petrochemical contamination of soil increased the abundance of isopods,[131] and chronic exposure to low concentrations of PAHs appeared to stimulate populations of several groups of soil invertebrates.[132] In soil remediation studies earthworms have been found to be a sensitive indicator of soil quality.[133]

In short-term exposure trials (24 to 96 h) on selected aquatic invertebrates, individual PAH compounds had LC_{50} values in water ranging from 0.1 to 5.6 ppm.[2,7] Eggs and larvae are more sensitive than juveniles or adults to dissolved PAHs. Larvae with a high tissue burden of PAHs from maternal transfer are likely to be at risk for increased toxicity from ultraviolet radiation.[134] Sublethal effects include reduced reproduction, inhibited development of embryos and larvae, delayed larval emergence, decreased respiration and heart rate, abnormal blood chemistry, and lesions.[2,7]

14.5.4 Fish

Adult and juvenile fish, larvae, and eggs are exposed to petroleum through contact with whole oil, dissolved hydrocarbons, particles of oil dispersed in the water column, or ingestion of contaminated food and water.[135,136]

Death of fish in natural habitat usually requires a heavy exposure to petroleum. Consequently, it is unlikely that large numbers of adult fish inhabiting large bodies of water would be killed by the toxic effects of petroleum. Fish kills usually are caused by large amounts of oil moving rapidly into shallow waters.[137,138] However, fresh and weathered crude oils and refined products vary considerably in their composition and toxicity, and the sensitivity of fish to petroleum differs among species. Petroleum concentrations (total petroleum hydrocarbons) in water of less than 0.5 ppm during long-term exposure[139] or higher concentrations (several to more than 100 ppm) in moderate- or short-term exposures can be lethal.[140–143] Sublethal effects begin at concentrations of less than 0.5 ppm and include changes in heart and respiratory rates, gill structural damage, enlarged liver, reduced growth, fin erosion, corticosteriod stress response, immunosuppression, impaired reproduction, increased external and decreased internal parasite burdens, behavioral responses, and a variety of biochemical, blood, and cellular changes.[136,142,144–154]

Eggs and larvae can suffer adverse effects, including death, when exposed to concentrations of petroleum in water ranging from less than 1 ppb (total PAHs) up to 500 ppb (total PAHs or total petroleum hydrocarbons).[155–158] Eggs, larvae, and early juveniles are generally more vulnerable than adults to oil spills and discharges because they have limited or no ability to avoid the oil, and they reside in locations that receive the most severe exposures (near the water surface or in shallow nearshore areas and streams). Effects of oil on eggs and larvae include death of embryos and larvae, abnormal development, reduced growth, premature and delayed hatching of eggs, DNA alterations, and other cellular abnormalities.[136,156–161] Evidence of continued adverse effects on the viability of pink salmon (*Oncorhynchus gorbuscha*) embryos for 4 years after the *Exxon Valdez* oil spill in Prince William Sound, Alaska, presented the possibility of gametic damage to exposed fish.[162]

Assessing the effect of petroleum spills and discharges on fish populations has been attempted with a variety of approaches, including taking fish samples from oiled and control areas after a spill,[163] monitoring postspill fish harvest and recruitment,[138] aerial surveys of fish stocks before and after spill events,[164] translating abundance of benthic prey into estimates of demersal fish biomass,[104] using a life-history model to estimate effects on a species,[165] measuring differences in fish community composition above and below a discharge site on a stream,[149] and evaluating the potential of deleterious heritable mutations induced by a one-time spill event to produce measurable population change.[166] Several of these attempts revealed likely effects of petroleum on fish populations.

Also, the potential effects of oil spills on regional pelagic fish populations were evaluated with an extensive modeling effort of the Georges Bank fishery off the northeastern coast of the United States.[167,168] Unfortunately, normal variation in natural mortality of eggs and larvae for such species as Atlantic cod (*Gadus morhua*), haddock (*Melanogrammus aeglefinus*), and Atlantic herring (*Clupea harengus*) is often larger than mortality estimates for the largest of spills. Consequently, direct field observations would not be able to distinguish the effect of a major oil spill on a single year class from natural variation in recruitment. The authors concluded that a comprehensive recruitment model was needed to separate the effect of spilled oil from expected natural mortality.

In general, it is difficult to determine the effect of an ephemeral petroleum discharge on fish populations in large bodies of water. It is beneficial to have before-and-after data, and some modeling appears necessary to identify effects that are difficult to measure. Also, time and geographic scale are important considerations in any population assessment.

In short-term exposure trials (24 to 96 h) on selected species of fish, individual PAH compounds had LC_{50} values in water ranging from 1.3 to 3400 ppb.[2] The primary target organ for toxic action is the liver. Sublethal effects on eggs, larvae, juveniles, and adult fish[2] are generally similar to those previously described for exposure to fresh or weathered petroleum and separate aromatic fractions but with greater emphasis on neoplasm induction and DNA alteration.

Induction of precancerous cellular changes in laboratory studies with PAHs and high frequencies of lesions and cancerous and noncancerous neoplasms in bottom-dwelling fish from areas contaminated with PAHs provide support for a causal relation between PAHs in sediment and the presence of cancer in several species of bottom-dwelling marine fish.[7,33,55,56,169–171] Fish from Puget Sound, Washington,[172] tributaries of southern Lake Erie, Ohio,[55,173,174] and the Elizabeth River, Virginia,[175] had cancerous and noncancerous skin and liver neoplasms, fin erosion, and a variety of other external abnormalities. Concentrations of total PAHs in the sediment were sometimes > 100 ppm and 50 to 10,000 times greater than in reference areas.[2,55,173,175]

There is evidence that exposure to high concentrations of PAHs can affect fish populations and communities. Lesion frequency, overall health assessment, and population age structure were useful biological measures for differentiating a population of brown bullheads (*Ameiurus nebulosus*) in an industrialized urban river (Schuylkill River, Philadelphia, Pennsylvania) from a population in a nonindustrialized suburban pond (Haddonfield, New Jersey).[176] Analysis of fish community structure revealed lower species diversity for contaminated Lake Erie tributaries (Black and Cuyahoga Rivers, Ohio) than for a reference stream (Huron River, Ohio).[174]

Metabolism of PAHs by feral fish in areas chronically contaminated with multiple pollutants is poorly studied; studies such as van der Oost[177] are rare. Also lacking is information on dose-effect and temporal aspects of *in situ* exposure to carcinogens.[33,55] Species differences in PAH metabolism and incidence of neoplasms, even among closely related species,[33] further complicate efforts to generalize about findings from individual studies.

14.5.5 Reptiles and Amphibians

The response of reptiles and amphibians to petroleum exposure is not well characterized. Various species of reptiles and amphibians were killed by a spill of bunker C fuel oil in the St. Lawrence River (E.S. Smith, New York Department of Environmental Conservation, Albany, NY, unpublished report). Sea snakes were presumed to have been killed by crude oil in the Arabian Gulf.[178] Petroleum could have been a contributing factor in the deaths of sea turtles off the coast of Florida,[179] in the

Gulf of Mexico following the *Ixtoc I* oil spill,[180] and in the Arabian Gulf after the Gulf War oil spills,[181] but the cause of death was not determined. Ingestion of oil and plastic objects has been reported for green (*Chelonia mydas*), loggerhead (*Caretta caretta*), and Atlantic Ridley (*Lepidochelys kempi*) turtles.[179,180,182]

Experimental exposure of juvenile loggerhead turtles to crude oil slicks revealed effects on respiration, skin, blood characteristics and chemistry, and salt gland function.[183] Juvenile loggerhead turtles were exposed to artificially weathered crude oil for 4 days followed by an 18-day recovery period; blood abnormalities and severe skin and mucosal changes from exposure were reversed during the recovery period.[184] Atlantic Ridley and loggerhead embryos died or developed abnormally when the eggs were exposed to oiled sand; weathered oil was less harmful to the embryos than fresh oil (T.H. Fritts and M.A. McGehee, Fish and Wildlife Service, Denver Wildlife Research Center, Denver, CO, unpublished report).

Bullfrog tadpoles (*Rana catesbeiana*) were exposed to amounts of No. 6 fuel oil that could be expected in shallow waters following oil spills; death was most common in tadpoles that were in the late stages of development, and sublethal effects included grossly inflated lungs, fatty livers, and abnormal behavior.[185] Larvae of the wood frog (*Rana sylvatica*), the spotted salamander (*Ambystoma maculatum*), and two species of fish were exposed to several fuel oils and crude oils in static and flow-through tests; sensitivity of the amphibian larvae to oil was slightly less than that of the two species of fish.[140] Exposure of green treefrog (*Hyla cinerea*) embryos and larvae and larval mole salamanders (*Ambystoma opacum* and *A. tigrinum*) to used motor oil in natural ponds, field enclosures, or laboratory containers caused reduced growth or reduced food (algae) densities and prevented metamorphosis of green frogs at high exposure.[186,187]

The injection or implantation in amphibians of perylene or crystals of benzo(a)pyrene and 3-methylcholanthrene induced cancerous and noncancerous tissue changes.[2] It has been suggested that amphibians are more resistant to PAH carcinogenesis than mammals because of the demonstrated inability of the hepatic microsomes of the tiger salamander (*A. tigrinum*) to produce mutagenic metabolites.[188] The toxicity and genotoxicity of benzo(a)pyrene and refinery effluent to larval newts (*Pleurodeles waltlii*), in the presence and absence of ultraviolet radiation, was established in a series of experiments by Fernandez and l'Haridon.[189]

14.5.6 Birds

Birds can be affected by petroleum through external oiling, ingestion, egg oiling, and habitat changes. External oiling disrupts feather structure, causes matting of feathers, and produces eye and skin irritation. Death often results from hypothermia and drowning.[1,190–192] Bird losses in excess of 5000 individuals are common for moderate to large petroleum spills. Birds that spend much of their time in the water, such as alcids (*Alcidae*), waterfowl (*Anatidae*), and penguins (*Spheniscidae*), are the most vulnerable to surface oil.

Petroleum can be ingested through feather preening, consumption of contaminated food or water, and inhalation of fumes from evaporating oil. Ingestion of oil is seldom lethal, but it can cause many debilitating sublethal effects that promote death from other causes, including starvation, disease, and predation. Effects include gastrointestinal irritation, pneumonia, dehydration, red blood cell damage, impaired osmoregulation, immune system suppression, hormonal imbalance, inhibited reproduction, retarded growth, and abnormal parental behavior.[192–203]

Bird embryos are highly sensitive to petroleum. Contaminated nest material and oiled plumage are mechanisms for transferring oil to the shell surface. Small quantities (1 to 20 μL) of some types of oil (light fuel oils, certain crude oils) are sufficient to cause death, particularly during the early stages of incubation.[204,205] Eggshell applications of petroleum weathered for several weeks or longer are less toxic to bird embryos than fresh or slightly weathered petroleum.[206,207]

Petroleum spilled in avian habitats can have immediate and long-term effects on birds. Fumes from evaporating oil, a shortage of food, and cleanup activities can reduce use of an affected area.[208,209]

Long-term effects are more difficult to document, but severely oiled wetlands and tidal mud flats are likely to have altered plant and animal communities for many years after a major spill.[62,82]

The direct and indirect effects of oil spills are difficult to quantify at the regional or species level. Death from natural causes and activities of humans (e.g., commercial fishing), weather, food availability, and movement of birds within the region can obscure the effects of a single or periodic catastrophic event. Regional population assessments in the northern Gulf of Alaska for bald eagles (*Haliaeetus leucocephalus*) and common murres (*Uria aalge*) after the *Exxon Valdez* oil spill in March 1989 failed to identify population changes attributable to the spill.[210–212] During the last 50 years seabird populations of western Europe have increased or decreased without apparent relation to losses from oil spills.[213,214]

Effects of oil spills are most likely to be detected at the level of local populations. Also, measures of survival, reproduction, and habitat use of numerous individual birds can be extrapolated to local or regional populations. The *Exxon Valdez* oil spill in Prince William Sound, Alaska caused the loss of an estimated 250,000 to 375,000 birds.[215,216] Adverse effects of this spill have been described for individuals of several species of seabirds or wintering waterfowl in Prince William Sound and extrapolated to populations.[217–220] Wiens et al.[218] also combined the species effects into assessments of avian community composition. Marine bird population declines have also been reported after the 1996 *Sea Empress* spill off the coast of England[221] and the 1991 Arabian Gulf oil spill.[222] Most of the changes in performance measures or local population size were no longer detectable by 2 years after the spill; exceptions were described by Wiens et al.,[218] Esler et al.,[221] and Symens and Suhaibani.[222]

The consequences of direct and indirect effects of oil spills on seabird populations have also been estimated with simulation models.[223–226] Models have shown that (1) an occasional decrease in survival of breeding adults will have a greater effect on seabird populations than an occasional decrease in reproductive success, (2) long-lived seabirds with low reproductive potential will have the most difficulty recovering from a catastrophic oil spill, and (3) recovery of a seriously depleted population of long-lived seabirds will be greatly hindered if adult survival and reproduction show small, but sustained, decreases. The overall recovery potential for a species depends on the reproductive potential of the survivors and the immigration potential from surrounding areas.[227,228]

Much of the available information on effects of PAHs on birds was produced by studies of the effects of petroleum on eggs. Experiments have shown that the PAH fraction of crude and refined oils is responsible for the lethal and sublethal effects on bird embryos caused by eggshell oiling.[205] Further, the toxicity of PAHs to bird embryos is a function of the quantity and molecular structure of the PAHs.[229] Brunstrom et al.[230] injected a mixture of 18 PAHs (2.0 mg/kg of egg) into eggs of the chicken (*Gallus domesticus*), turkey (*Meleagris gallopavo*), domestic mallard (*Anas platyrhynchos*), and common eider (*Somateria mollissima*) and found the mallard to be the most sensitive species and benzo[k]fluoranthene (four rings) and indeno[1,2,3-cd]pyrene (five rings) to be the most toxic of the PAHs tested. The most toxic PAHs were found to have additive effects on death of embryos, and the cause of toxicity was proposed to be a mechanism controlled by the Ah receptor.[231] Naf et al.[232] injected a mixture of 16 PAHs (0.2 mg/kg of egg) into chicken and common eider eggs and reported that > 90% was metabolized by day 18 of incubation (chicken), with the greatest concentration of PAHs in the gall bladder of both species. Mayura et al.[233] injected fractionated PAH mixtures from coal tar (0.0625 to 2.0 mg/kg of egg) into the yolk of chicken eggs and found that death, liver lesions and discoloration, and edema increased as the proportion of five- and > five-ring aromatics, compared to the proportion of two- to four-ring aromatics, increased in the mixture.

Studies with adults and nestlings revealed a variety of sublethal toxic effects induced by PAHs. Male mallard ducks fed 6000 ppm of a mixture of 10 PAHs combined with 4000 ppm of a mixture of 10 alkanes for 7 months in a chronic ingestion study had greater hepatic stress responses and higher testes weights than male mallards fed 10,000 ppm of the alkane mixture.[234] Nestling herring gulls (*Larus argentatus*) were administered single doses (0.2 or 1.0 mL) of crude oils, their aromatic or aliphatic fractions, or a mixture of crude oil and dispersant.[235,236] Retardation of nestling weight gain and increased adrenal and nasal gland weights was attributed to the PAHs with four or more rings. Immune function and mixed-function oxidase activity of adult European starlings (*Sturnus vulgaris*) were altered by subcutaneous injections (25 mg/kg body weight) of 7,12-dimethylbenz[a]anthracene, a four-ring PAH, every other day for 10 days.[237] Oral doses in adult birds (25 mg/kg body weight) and nestlings (20 mg/kg body weight) also altered immune function. The coefficient of variation of nuclear DNA volume of red blood cells from wild lesser scaup (*Athya affinis*) was positively correlated with the concentration of total PAHs in scaup carcasses.[238]

14.5.7 Mammals

Marine mammals that rely primarily on fur for insulation, such as the sea otter (*Enhydra lutris*), polar bear (*Ursus maritimus*), Alaska fur seal (*Callorhinus ursinus*), and newborn hair seal pups (*Phocidae*), are the most likely to die after contact with spilled oil.[22,239,240] Oiled fur becomes matted and loses its ability to trap air or water, resulting in hypothermia. Adult hair seals, sea lions (*Eumetopias jubatus, Zalophus californianus*), and cetaceans (whales, porpoises, dolphins) depend primarily on layers of fat for insulation; thus, oiling causes much less heat loss. However, skin and eye irritation and interference with normal swimming can occur. Skin absorption of oil has been reported for seals and polar bears.

Oil ingested in large quantities can have acute effects on marine mammals. However, marine mammals, such as seals and cetaceans, are capable of rapid hydrocarbon metabolism and renal clearance.[239] Ingested oil can cause gastrointestinal tract hemorrhaging in the European otter (*Lutra lutra*);[241] renal failure, anemia, and dehydration in the polar bear;[242] pulmonary emphysema, centrilobular hepatic necrosis, hepatic and renal lipidosis, increased nuclear DNA mass, altered blood chemistry, and possible gastric erosion and hemorrhage in sea otters,[243–245] and altered blood chemistry and reduced body weight in river otters (*Lontra canadensis*).[246] Inhalation of evaporating oil is a potential respiratory problem for mammals near or in contact with large quantities of unweathered oil.[239,247] Some of the previously described disorders are thought to be caused by hypothermia, shock, and stress rather than direct toxic action; distinguishing between the two types of causes can be difficult.[248]

Effects of the *Exxon Valdez* oil spill on populations of sea otter, harbor seals (*Phoca vitulina*), Stellar sea lions, killer whales (*Orcinus orca*), and humpback whales (*Megaptera novaeangliae*) in Prince William Sound, Alaska, are summarized in the overview provided by Loughlin et al.[245] Sea otters and harbor seals were the most affected, with loss estimates in the thousands for otters and in the hundreds for seals. Age distributions of dead sea otters systematically collected from oiled areas of western Prince William Sound between 1976 and 1998 revealed a reduction in the survival rate of otters during the 9 years after the spill (1990–1998).[249] Aerial counts of harbor seals at seven sites affected by the oil spill and 18 unaffected sites in central and eastern Prince William Sound revealed a 28% population reduction during the period 1990–1997; however, harbor seal populations on the survey route were declining prior to the 1989 spill.[250] Effects of the Gulf War oil spills on cetaceans in the Arabian Gulf were thought to be minimal.[251] Overall, the consequences of local effects (acute, chronic, and indirect) of catastrophic oil spills on regional populations of marine mammals have proven difficult to determine because of a lack of prespill population information, movement of animals within the region, and natural fluctuations in survival and reproduction.

Documentation of the effects of oil spills on wild nonmarine mammals is less than for marine mammals. Large numbers of muskrats (*Ondatra zibethica*) were killed by a spill of bunker C fuel oil in the St. Lawrence River (E.S. Smith, New York Department of Environmental Conservation, Albany, NY, unpublished report). Giant kangaroo rats (*Dopodomys ingens*) in California were found dead after being oiled,[252] beaver (*Castor canadensis*) and muskrats were killed by an aviation kerosine spill in a Virginia river,[253] and rice rats (*Oryzomys palustris*) in a laboratory experiment died after swimming through oil-covered water.[254] Oil field pollution in wooded areas in Russia affected blood characteristics, organ indices, species composition, relative abundance, and population age and sex structure of small mammals.[255] Cotton rats occupying old petrochemical sites were characterized by increased cell apoptosis in the ovary and thymus,[256] and rodent populations and assemblages on the same types of sites were altered compared to nearby reference sites.[257] The literature on effects of crude or refined petroleum on laboratory and domestic animals is substantial; recent examples are Lee and Talaska (DNA adduct formation in mouse skin),[258] Feuston et al. (systemic effects of dermal application in rats),[259] Khan et al. (clinical and metabolic effects in dosed cattle),[260] and Mattie et al. (pathology and biochemistry of dosed rats).[261]

The effects of major oil spills on the environment of mammals could include food reduction, an altered diet, and changed use of habitat.[262,263] These effects could be short- or long-term and would be most serious during the breeding season, when movement of females and young is restricted.

The metabolism and effects of some PAHs have been well documented in laboratory rodents and domestic mammals but poorly documented in wild mammals. Acute oral LD_{50} values for selected PAHs in laboratory rodents range from 50 to 2000 mg/kg body weight.[2] Target organs for PAH toxic action are skin, small intestine, kidney, and mammary gland; tissues of the hematopoietic, lymphoid, and immune systems; and gametic tissue. Nonalkylated PAHs are rapidly metabolized; hence, accumulation is less likely than for alkylated PAHs.[2] Partially aromatic PAHs, alkylated fully and partially aromatic PAHs, and metabolites of nonalkylated, fully aromatic PAHs have the greatest potential to alter DNA and induce cancerous and noncancerous neoplasms in epithelial tissues of laboratory and domestic mammals.[2] Species differences in sensitivity to carcinogenesis appears to be a function of differences in levels of mixed-function oxidase activities. Background exposure concentrations of PAHs and studies on mixtures of PAHs in mammals are needed to accurately assess the potential hazard of exposure to multiple PAHs in polluted environments.[2]

Although PAHs can produce systemic effects, DNA alterations, and cancer, concerns about the carcinogenic and mutagenic potential predominate, especially for human health. Consequently, PAHs that are carcinogenic or mutagenic are most studied.[2] With regard to wild mammals, a few investigations have documented the presence of PAH adducts on DNA of marine mammals,[264–266] and participants of a recent workshop on marine mammals and persistent ocean contaminants[267] described PAHs as a "less widely recognized" contaminant that should be further studied because of potential mutagenic and genotoxic effects.

14.5.8 The *Exxon Valdez* and Arabian Gulf Oil Spills

The 1989 *Exxon Valdez* oil spill (EVOS) in Prince William Sound, Alaska and the Gulf War oil spills (GWOS) in the Arabian Gulf in 1991 are worthy of special comment. Each was significant for different reasons, and reports of the fate and effects of these spills dominated the petroleum pollution literature during the 1990s.

The EVOS consisted of 36,000 metric tons of crude oil released in just a few days into a high-latitude, relatively pristine marine ecosystem. Although many times smaller than the Gulf War oil discharges, the scientific and societal response was immediate and intense. The spill resulted in a massive oil-removal effort,[268] a thorough crude oil mass balance determination spanning the period 3/24/89 to 10/1/92[269] and the largest wildlife rescue and rehabilitation effort ever attempted (at a cost of $45 million).[270]

In the United States, the Clean Water Act and the Comprehensive Environmental Response, Compensation, and Liability Act determined the response requirements for trustees (federal, state, tribal) of affected natural resources. Trustees initiated research that sought evidence of "injury" to natural resources, and Exxon Corporation initiated research that sought to demonstrate minimal injury and subsequent restoration of affected resources. This adversarial legal process discouraged cooperation among scientists and delayed public access to the results of the studies for several years.[268] Two books containing studies sponsored mostly by Exxon[271] and Trustees[272] provide many examples of conflicting interpretations of the effects of the spill; Wiens[273] provides a discussion of the effects of advocacy on investigations of the effects of the spill on birds. The EVOS is rapidly becoming the most studied oil spill in history; a stream of scientific reports continues to be generated by scientists assessing the biological consequences.

The GWOS consisted of 240 million metric tons of crude oil released into the northern Arabian Gulf over a 6-month period; the Gulf had a previous history of petroleum pollution from oil production activities and warfare. The spillage was caused by acts of war, and scientific coverage of the progression of the spill and its biological effects was delayed until hostilities ended and munitions were cleared from areas affected by discharged oil. Investigators from a number of countries performed assessments of the effects of the oil, which appear to have been less severe on plants and animals of aquatic and coastal environments than the effects reported for the EVOS. In contrast, the contamination of terrestrial environments caused by destruction of oil wells and pipelines was severe and is likely to affect terrestrial plants and animals for many years to come.[274,275]

14.5.9 Conclusions

The effects of petroleum on organisms are as varied as the composition of petroleum and the environmental conditions accompanying its appearance. Petroleum can cause environmental harm by toxic action, physical contact, chemical and physical changes within the soil or water medium, and habitat alteration. Oil spills have caused major changes in local plant and invertebrate populations lasting from several weeks to many years. Effects of oil spills on populations of mobile vertebrate species, such as fish, birds, and mammals, have been difficult to determine beyond an accounting of immediate losses and short-term changes in local populations. Reptiles and amphibians need further study. Knowledge of the biological effects of petroleum in freshwater environments continues to increase but still lags behind comparable information for saltwater environments.

Concentrations of individual PAHs in air, soil, and water are usually insufficient to be acutely toxic, but numerous sublethal effects can be produced. The induction of lesions and neoplasms in laboratory animals by metabolites of PAHs and observations of lesions and neoplasms in fish from PAH-contaminated sites indicate potential health problems for animals with a strong MFO system capable of metabolizing PAHs. Although evidence linking environmental PAHs to the incidence of cancerous neoplasms in wild vertebrates is primarily limited to fish, the growing quantities of PAHs entering our environment are a cause for concern.

14.6 SUMMARY

Petroleum and individual PAHs from anthropogenic sources are found throughout the world in all components of ecosystems. Crude and refined oils are highly variable in composition and physical characteristics and consist of thousands of hydrocarbon and nonhydrocarbon compounds. Polycyclic aromatic hydrocarbons are aromatic hydrocarbons with two to seven fused benzene rings that can have alkyl groups attached to the rings. Less than half of the petroleum in the environment comes from spills and discharges associated with petroleum transportation. Most of the petroleum comes from industrial, municipal, and household discharges; motorized vehicles; natural oil seeps; and acts of war, terrorism, vandalism, and theft. Most PAHs are formed by a process of thermal decomposition and subsequent recombination of organic molecules (pyrolysis and pyrosynthesis). Low-temperature processes produce the PAHs in coal and oil. High-temperature processes can occur naturally (forest and grass fires, volcanoes) or can be caused by anthropogenic activities (oil, coal, and wood combustion; refuse incineration; industrial activity). Most high-temperature PAHs enter the environment as combustion emissions or components of liquid waste effluents from industrial sites and municipal sewage plants.

Crude and refined petroleum spreads rapidly on water and begins to change composition upon exposure to air, water, or sunlight. Anthropogenic aromatic hydrocarbons are dispersed by air currents and movement of waters receiving wastewater effluents. Hydrocarbons are primarily degraded by microbial metabolism; mammals, birds, fish, and many macroinvertebrates can also metabolize ingested hydrocarbons. Hydrocarbons are also degraded by photooxidation, photolysis, and chemical oxidation.

Organisms with high lipid content, activity patterns or distributions that coincide with the location of the hydrocarbon source, and a poor mixed-function oxygenase system are most likely to accumulate hydrocarbons. Trophic-level increases in accumulation have not been observed. Residence time for petroleum in the water column is usually less than 6 months. Coastal environments can retain oil from several days to 20 years, depending on the configuration of the shoreline, type of substrate, and climate. High-molecular-weight hydrocarbons, particularly aromatics, can persist for long periods of time (> 20 years) in sediments and terrestrial soils.

Petroleum can have lethal or sublethal effects in plants and microbes. Recovery from the effects of oil spills requires as little as a few weeks for water column microalgae up to 5 years for most wetland plants; mangroves could require up to 20 years. Individual PAHs at low concentrations can induce positive or negative sublethal effects in aquatic bacteria and algae; high concentrations can lead to death.

Oil spills often have pronounced effects on local populations of invertebrates; recovery could require a week for zooplankton or 10 years for intertidal populations of mollusks. A large and diverse amount of experimental and survey research, performed with saltwater and freshwater invertebrates, has demonstrated lethal and many sublethal effects as well as population and community effects. Individual PAHs can be lethal at high concentrations and cause sublethal effects at low concentrations.

Eggs, larvae, and early juvenile stages of fish are more vulnerable to oil because they have limited or no ability to avoid it. Large losses of adult fish are usually limited to situations where a large quantity of oil rapidly moves into shallow water. Many sublethal effects of oil on fish have been documented. Effects of oil spills on fish populations in large bodies of water are difficult to determine because of large natural variation in annual recruitment. Laboratory studies of PAH metabolism and lesions and tumors in fish collected from areas heavily contaminated with PAHs imply that PAH exposure can cause cancerous and noncancerous tissue changes in feral fish. Uncertainties about the interactive effects of multiple pollutants at heavily contaminated sites and inadequate knowledge of dose-effect responses and temporal aspects of *in situ* exposure to carcinogens complicate efforts to link environmental PAHs to neoplasms or local population changes.

Adult reptiles and amphibians can be killed and their eggs and amphibian larvae killed or sublethally affected by petroleum. However, available information is inadequate to compare their sensitivity to petroleum or individual PAHs to that of other vertebrates.

Birds are often killed by oil spills, primarily because of plumage oiling and oil ingestion. Birds that spend much of their time on the water surface are the most vulnerable to spilled oil. Ingested oil can cause many sublethal effects. Effects of oil spills are more likely to be detected at the level of local populations than at the regional or species level. When the quantity of data is large, investigators often extrapolate responses of individual birds to local and regional populations. Population modeling studies have shown that long-lived birds with low reproductive success will have the most difficulty recovering from a major oil spill. Recovery potential for a species is a function of the reproductive potential of the survivors and the immigration potential at the spill site. Experiments with individual or groups of PAHs and bird eggs, nestlings, and adults have revealed a variety of toxic responses and shown that PAHs are responsible for most of the toxic effects attributed to petroleum exposure.

Mammals that rely on fur for insulation (polar bear, otters, fur seals, muskrat) are the most likely to die from oiling. Mammals that rely on layers of fat for insulation (seals, cetaceans) are infrequently killed by oil. Ingested oil is rapidly metabolized and cleared, but it can cause many sublethal effects. Effects of spilled oil on local and regional populations of marine mammals have proven difficult to determine because of a lack of prespill population information, movement of animals within the region, and natural fluctuations in survival and reproduction. Laboratory mammals, but not wild mammals, have been extensively used to study the toxic and carcinogenic potential of individual PAHs. Partially aromatic PAHs, alkylated, fully and partially aromatic PAHs, and metabolites of nonalkylated, fully aromatic PAHs have the greatest potential to cause neoplasms in tissues of laboratory and domestic mammals. Investigations involving mixtures of PAHs are especially needed.

In general, petroleum negatively affects living organisms through physical contact, toxic action, and habitat modification, whereas individual PAHs have toxic effects. Partially metabolized and alkylated PAHs can induce genetic damage, developmental abnormalities, and cancerous and noncancerous tissue changes. Evidence linking environmental concentrations of PAHs to induction of cancer in wild animals is strongest for fish. Although concentrations of individual PAHs in aquatic environments are usually much lower than concentrations that are acutely toxic to aquatic organisms, sublethal effects can be produced. Effects of spills on populations of mobile species have been difficult to determine beyond an accounting of immediate losses and, sometimes, short-term changes in local populations.

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REAL-TIME RELIABILITY ASSESSMENT & MANAGEMENT OF MARINE PIPELINES

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ABSTRACT

In-line instrumentation information processing procedures have been developed and implemented to permit 'real-time' assessment of the reliability characteristics of marine pipelines. The objective of this work is to provide pipeline engineers, owners and operators with additional useful information that can help determine what should be done to help maintain pipelines.

This paper describes the real-time RAM (reliability assessment and management) procedures that have been developed and verified with results from laboratory and field tests to determine the burst pressures of pipelines. These procedures address the detection and accuracy characteristics of results from in-line or 'smart pig' instrumentation, evaluation of the implications of non-detection, and the accuracy of alternative methods that can be used to evaluate the burst pressures of corroded and dented – gouged pipelines.

In addition, processes are described have been developed to permit use of the information accumulated from in-line instrumentation (pipeline integrity information databases) to make evaluations of the burst pressure characteristics of pipelines that have not or can not be instrumented.

Both of these processes are illustrated with applications to two example pipelines; one for which in-line instrumentation results are available and one for which such information is not available.

Keywords: Pipelines, Reliability, Instrumentation

INTRODUCTION

Pipeline in-line instrumentation has become a primary means for gathering detailed data on the current condition of pipelines. It would be very desirable for the pipeline owner, operator, and regulator to have a highly automated process to enable preliminary assessment of the reliability of the pipeline in its current and projected future conditions (Fig. 1)

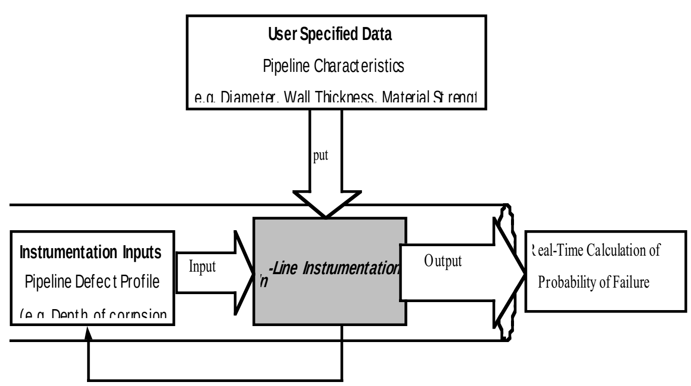

Fig. 1: Real-Time RAM process

Pipeline in-line instrumentation data can provide a large amount of data on damage and defects (features) in a pipeline. This data must be properly interpreted before the features can be characterized. The detection of features varies as a function of the size and geometry of the features, the in-line instrumentation used, and the characteristics and condition of the pipeline. Given results from in-line instrumentation, it is desirable to develop a rapid and realistic evaluation of the effects of the detected features on the pipeline integrity. This evaluation requires and analysis of how the detected features might affect the ability of the pipeline to maintain containment.

RELIABILITY FORMULATION

The Reliability Assessment and Management (RAM) formulation used in this development is based on a probabilistic approach based on Lognormal distributions for both pipeline demand and capacity distributions. Such distributions have been shown to provide good approximations to the 'best-fit' distributions, particularly when the tails of the Lognormal distributions are fitted to the region of the distributions that have the greatest influence on the probability of failure. The Lognormal formulation for the probability of failure (Pf) is:

$$Pf = 1 - \Phi\left[\frac{\ln\left(\frac{R_{50}}{S_{50}}\right)}{\sigma_{\ln RS}}\right] = 1 - \Phi[\beta]$$

Φ is the Cumulative Normal Distribution for the quantity [•]. R_{50} is the median capacity. S_{50} is the median demand. The ratio of R_{50} to S_{50} is known as the median or central Factor of Safety (FS_{50}). $\sigma_{\ln RS}$ is the standard deviation of the logarithms of the capacity (R) and demand (S):

$$\sigma_{\ln RS} = \sqrt{\sigma^2_{\ln R} + \sigma^2_{\ln S}}$$

$\sigma_{\ln R}$ is the standard deviation of the capacity and $\sigma_{\ln S}$ is the standard deviation of the demand. For coefficients of variation (V_X = ratio of standard deviation to mean value of variable X) less than about 0.5, the coefficient of variation of a variable is approximately equal to the standard deviation of the logarithm of the variable. The quantity in brackets is defined as the Safety Index (β). The Safety Index β is related approximately to Pf as $1 \leq \beta \leq 3$):

$$Pf \approx 0.475 \exp -(\beta)^{1.6}$$

The results of this development are summarized in Fig. 2. The probability of failure (loss of containment) is shown as a function of the central factor of safety (FS_{50}) and the total uncertainty in the pipeline demands and capacities (σ). Note that the probability of failure can be determined from two fundamental parameters: the central factor of safety ($FS_{50} = R_{50}/S_{50}$) and the total uncertainty in the demands and capacities ($\sigma_{\ln RS} = \sigma$).

TIME DEPENDENT RELIABILITY

When a pipeline is subjected to active corrosion processes, the probability of failure is a time dependent function that is dependent on the corroded thickness of the pipeline (tci/e). The corroded thickness is dependent on the rate of corrosion and the time that the pipeline or riser is exposed to corrosion.

Insight into the change in the uncertainty associated with the pipeline capacity associated with the loss of wall thickness due to corrosion, can be developed by the following:

$$\bar{t}' = \bar{t} - \bar{d}$$

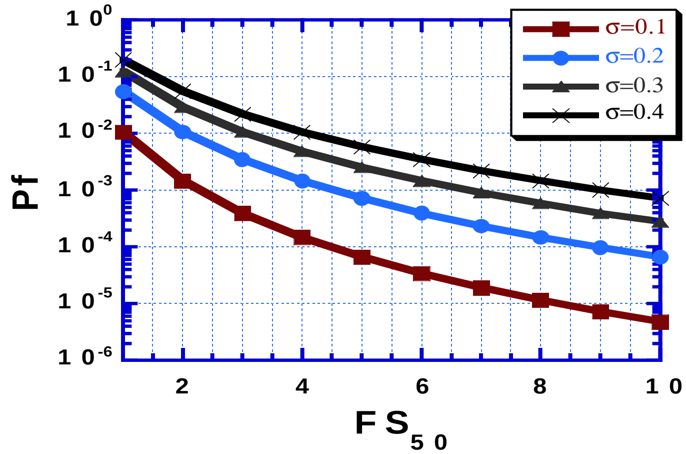

Fig. 2: Probability of failure as function of central Factor of Safety and total uncertainty

t' is the wall thickness after the corrosion, t is the wall thickness before corrosion, and d is the maximum depth of the corrosion loss. Bars over the variables indicate mean values.

Based on First Order – Second Moment methods, the standard deviation of the wall thickness after corrosion can be expressed as:

$$\sigma_{t'} = \sqrt{\sigma_t^2 + \sigma_d^2}$$

The Coefficient of Variation (COV = V) can be expressed as:

$$V_{t'} = \frac{\sigma_{t'}}{\bar{t}'} = \frac{\sqrt{(V_t \bar{t})^2 + (V_d \bar{d})^2}}{\bar{t} - \bar{d}}$$

A representative value for the COV of t would be 2%. A representative value for the COV of d would be Vd = 40%. Fig. 3 summarizes the foregoing developments for a 16-in. (406 mm) diameter pipeline with an initial wall thickness of t = 0.5 in. (17 mm) that has an average rate of corrosion of 10 mpy (0.010 in. / yr, 0.25 mm / yr). The dashed line shows the results for the uncertainties associated with the wall thickness. The solid line shows the results for the uncertainties that include those of the wall thickness, the prediction of the corrosion burst pressure, and the variabilities in the maximum operating pressure.

At the time of installation, the pipeline wall thickness COV is equal to 2%. But, as time develops, the uncertainties associated with the wall thickness increase due to the large uncertainties associated with the corrosion rate – maximum depth of corrosion. The solid line that reflects all of the uncertainties converges with the dashed line that represents the uncertainties in the remaining wall thickness, until at a time of about 20 years, the total uncertainty is about the same as that of the remaining wall thickness (Vt-d ≈ 25 %). As more time develops, there is a dramatic increase in the COV associated with the remaining wall thickness. These uncertainties are dominated by the uncertainties attributed to the corrosion processes.

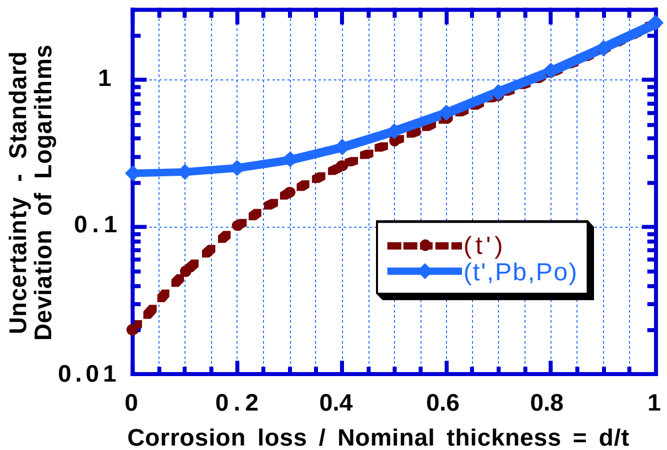

Fig. 3: Uncertainty in pipeline wall thickness and burst pressure capacity as a function of the normalized loss in pipeline wall thickness

These observations have important ramifications on the probabilities of failure – loss of containment of the pipeline. After the 'life' of the pipeline is exceeded (e.g. 20 to 25 years), one can expect there to be a rapid and dramatic increase in the uncertainties associated with the corrosion processes. In addition, there will be the continued losses in wall thickness. Combined, these two factors will result in a dramatic increase in the probability of failure of a pipeline.

Fig. 4 summarizes example results for a 16-in. (406 mm) diameter, 0.5 in (13 mm) wall thickness pipeline that has a maximum operating pressure (MOP) of 5,000 psi (34.5 Mpa). The COV associated with the MOP is 10%. The pipeline is operated at the maximum pressure, and at 60% of the maximum operating pressure for a life of 0 to 50 years. The average corrosion rate was taken as 10 mills per year (mpy). For the 60% pressured line, during the first 20 years, the annual probability of failure rises from 1E-7 to 5 E-3 per year. After 20 years, the annual probability of failure rises very quickly to values in the range of 0.1 to 1. Perhaps, this helps explain why the observed pipeline failure rates associated with corrosion in the Gulf of Mexico are in the range of 1 E-3 per year.

TRUNCATED DEMAND & CAPACITY DISTRIBUTIONS

Real-time RAM analytical models have been developed to allow determination of the effects of user specified truncations in pipeline demands, capacities; separately or combined.

The effect of pressure testing is to effectively 'truncate' the probability distribution of the pipeline burst pressure capacity below the test pressure (Fig. 5). Pressure testing is a form of 'proof testing' that can result in an effective increase in the reliability of the pipeline.

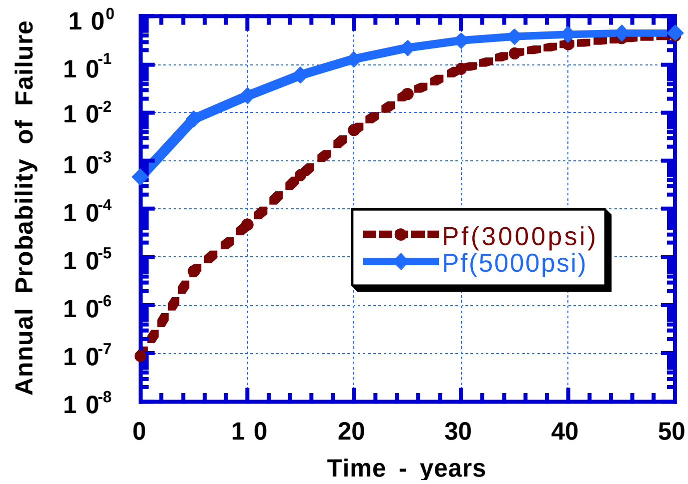

Fig. 4: Example pipeline failure rates as function of exposure to corrosion

There can be a similar effect on the operating pressure demands if there are pressure relief or control mechanisms maintained in the pipeline. Such pressure relief or control equipment can act to effectively truncate or limit the probabilities of developing very high unanticipated operating pressures (due to surges, slugging, or blockage of the pipeline).

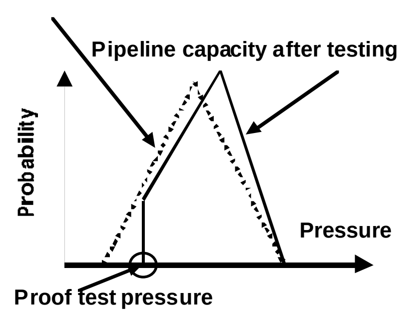

Fig. 5: Effects of proof testing on pipeline capacity distribution

This raises the issues associated with pressure testing and pressure controls on the computed probabilities of failure. It is important to note that such distribution truncation considerations have been omitted from all pipeline reliability based studies and developments that have been reviewed during the past 10 years of research on this topic.

Fig. 6 summarizes the results of pipeline proof testing on the pipeline Safety Index (the probability of loss of containment is $P_{lc} \approx 10^{-\beta}$) as a function of the 'level' of the proof testing pressure factor, K:

$$K = \ln (Xp / \mathbf{p}_b) / \sigma_{\ln pb}$$

where Xp / **pb** is the ratio of the test pressure to the median burst pressure capacity of the pipeline (test pressure deterministic, burst pressure capacity Lognormally distributed) and is the standard deviation of the Logarithms of the pipeline burst pressure capacities. These results have been generated for the case where the uncertainty associated with the maximum operating / incidental pressures is equal to the uncertainty of the pipeline burst pressures and for Safety Indices in the range of $\beta = 3$ to $\beta = 4.5$.

For example, if the median burst pressure of the pipeline were 2,000 psi and this had a Coefficient of Variation of 10 %, there was a factor of safety on this burst pressure of 2 (f = 0.5) (maximum operating pressure = 1,000 psi), and the pipeline was tested to a pressure of 1.25 times the maximum operating pressure (Xp = 1,250 psi), the proof testing factor K = -4.7. The results in Fig. 6, indicate that this level of proof testing is not effective in changing the pipeline reliability. Even if the pipeline were tested to a pressure that was 1.5 times the operating pressure, the change in the Safety Index would be less than 5 %.

If the test pressure were increased to 75% of the median burst pressure, the Safety Index would be increased by about 25 %. For a Safety Index of $\beta = 3.0$ (Pf = 1E-3), these results indicate a $\beta = 3.75$ (Pf = 1E-4) after proof testing.

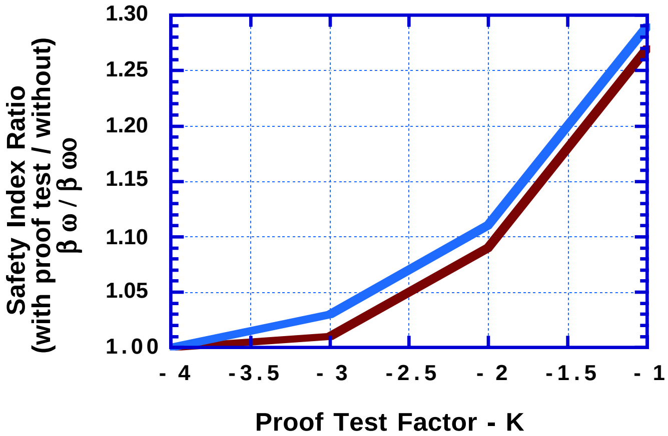

Fig. 6: Effects of proof testing on pipeline reliability

Very high levels of proof testing are required before there is any substantial improvement in the pipeline reliability. These results indicate that conventional pressure testing may not be very effective at increasing the burst pressure reliability characteristics. Such testing may be effective at disclosing accidental flaws incorporated into the pipeline (e.g. poor welding).

PROBABILITIES OF DETECTION

Fig. 7 shows results from inline Magnetic Flux Leakage (MFL) instrumentation of a 20-in (508 mm) diameter gas line in the Bay of Campeche (Pig C) [1]. The measured and corrected corrosion expressed as a percentage of the wall thickness is shown.

Fig. 8 summarizes data for two inline MFL instruments in which the in-line data on corrosion defect depths were compared with the corrosion defect depths determined from direct measurements on recovered sections of the pipeline that was in-line instrumented. For this particular condition, both in-line instruments tend to under estimate the corrosion depth. The uncertainties associated with the measured depths ranged from 35% (for 50 mils depths) to 25% (for 200 mils depths). The corrected wall thickness shown in Fig. 7 was based on these data.

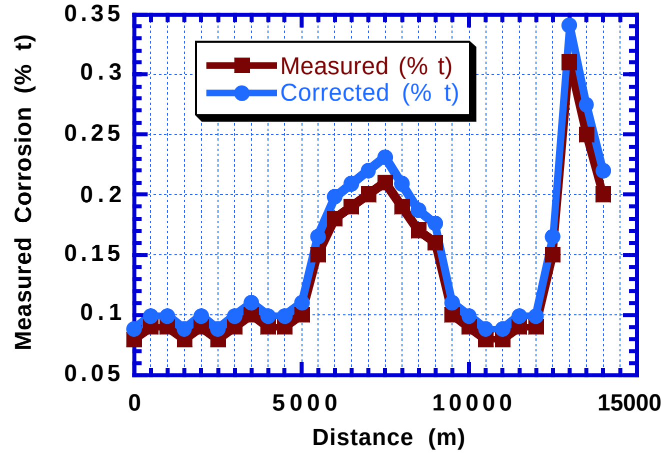

Fig. 7: Measured and corrected corrosion readings

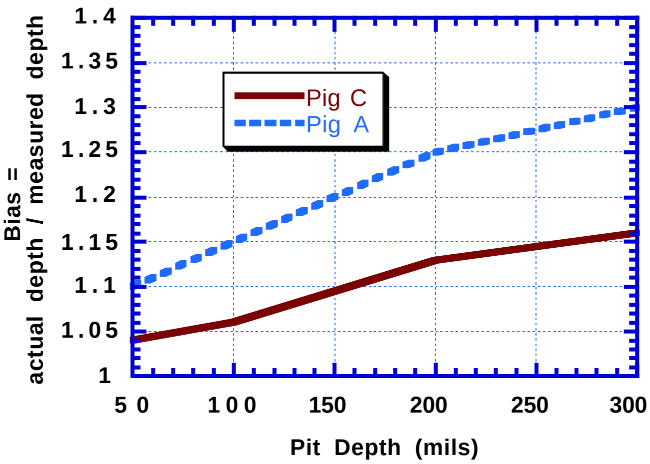

Fig. 8. Bias in measured corrosion depths

Based on using results from inline instrumentation, the probability of failure can be expressed as:

$$Pf = Pf_D + Pf_{ND}$$

where Pf_D is the probability of failure associated with the detected flaws and Pf_{ND} is the probability of failure associated with the non-detected flaws.It is important recognize that making evaluations of corrosion rates and wall thicknesses from the recordings have significant uncertainties/ Fig. 9 shows a comparison of the Probability of Detection (POD) of corrosion depths (in mils, 50 mils = 1.27 mm) developed by three different inline MFL instruments. This information was based on comparing measured results from sections of a pipeline that were repeatedly in-line instrumented and then retrieved and the directly measured corrosion depths determined. These are results from three similar MFL in-line instruments. However, there are significant differences in the POD. This indicates an important need to standardize in-line instrumentation and data interpretation.

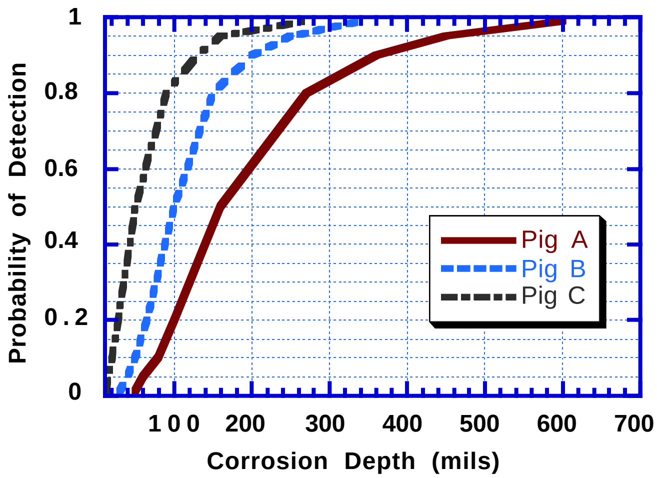

Fig. 9: Probability of detection curves for three in-line instruments

The probability of failure associated with the detected depth of corrosion can be expressed as:

$$Pf_D = 1 - \Phi\{[\ln(p_{B50}/p_{O50})]/[(\sigma^2_{pB}+\sigma^2_{pO})^{0.5}]$$

where p_{B50} is the 50th percentile (median) burst pressure, p_{O50} is the 50th percentile maximum operating pressure, σ_{pB} is the standard deviation of the logarithms of the burst pressure, and σ_{pO} is the standard deviation of the logarithms of the maximum operating pressures. The pipeline burst pressure is determined from the RAM PIPE formulation:

$$Pbd = 3.2\ t\ SMYS\ /\ Do\ SCF$$

$$SCF = 1 + 2\ (d\ /\ R)^{0.5}$$

where Pbd is the burst pressure capacity of the corroded pipeline, t is the nominal wall thickness (including the corrosion allowance), Do is the mean diameter (D–t), D is the pipeline outside diameter, SMYS is the specified minimum yield strength, and SCF is a stress concentration factor that is a function of the depth of corrosion, d (d≤t), and the pipeline radius, R.

The median of the burst pressure is determined from the medians of the variables. The uncertainty in the burst pressure is determined from the standard deviations of all of the variables:

$$\sigma^2_{\ln pB50} = \sigma^2_{\ln S} + \sigma^2_{\ln t} + \sigma^2_{\ln tc} + \sigma^2_{\ln D}$$

The probability of a corrosion depth, X, exceeding a lower limit of corrosion depth detectability, xo, is:

$$P[\ X \geq xo \mid ND\ ] =$$

$$P[\ X > xo\ ]\ P[\ ND \mid X \geq xo\ ]\ /\ P[\ ND]$$

P [X ≥ xo | ND] is the probability of no detection given X ≥ xo. P [X > xo] is the probability that the corrosion depth is greater than the lower limit of detectability. P [ND | X ≥ xo] is the probability of non detection given a flaw depth. P [ND] is the probability of non detection across the range of flaw depths where:

$$P[ND] = 1 - P[D]$$

and:

$$P[ND] = \Sigma\ P[ND \mid X > xo]\ P[X > xo]$$

The probability of failure for non-detected flaws is the convolution of:

$$Pf_{ND} = \Sigma\ [Pf \mid X > xo]\ P[\ X \geq xo \mid ND\ ]$$

Fig. 24 shows the probabilities of burst failure (detected and non-detected) of the pipeline. The majority of the pipeline has probabilities of failure of about 1 E-2 per year. However, there are two sections that have substantially higher probabilities of failure. One section is a low section in the pipeline where water can accumulate and the other is in the riser section that is subjected to higher temperatures and external corrosion. The probabilities of failure for these two sections are 1.7 E-2 and 2.9 E-2 per year, respectively. These two sections of the pipeline would be candidates for replacement.

ANALYTICAL MODEL BIAS

One of the most important parts of a reliability assessment is the evaluation of the Bias that is associated with various analytical models to determine the capacity of a pipeline. In this development, Bias is defined as the ratio of the true or measured (actual) loss of containment (LOC) pressure capacity of a pipeline to the predicted or nominal (e.g. code or guideline based) capacity:

$$\text{Bias} = B_X = \frac{\text{True}}{\text{Predicted}} = \frac{\text{Measured}}{\text{Nominal}}$$

It is important to note that the measured value determined from a laboratory experiment is not necessarily equal to the true or actual value that would be present in the field setting. Laboratory experiments involve 'compromises' that can lead to important differences between the true or actual pipeline capacity and that measured in the laboratory. For example, the end closure plates used on laboratory test specimens of pipelines will introduce axial stresses that can act to increase the LOC pressure capacity relative to a segment of the pipeline in the field in which there would not be any significant axial stresses.

One important example of the potential differences between the true pipeline capacity and the experimentally determine pipeline capacity regards laboratory experiments that are used to determine the burst pressure capacity of corroded pipelines. To facilitate the laboratory experiments (controlled parameter variations), the corroded features frequently are machined into the pipeline specimen. This machining process can lead to important differences between actual corroded features and those machined into the specimens; stress concentrations can be very different; residual stresses imparted by the machining process can be very different; and there can be metallurgical changes caused by the machining process. Thus, laboratory results must be carefully regarded and it must be understood that such experiments can themselves introduce Bias into the assessment of pipeline reliability.

Another important example regards true or 'measured' results that are based on results from analytical models. Such an approach has been used to generate 'data' used in several recent major reliability based code and guideline developments. The general approach is to use a few high quality physical laboratory tests to validate or calibrate the analytical model. Then the analytical model is used to generate results with the model's parameters being varied to develop experimental data. One colleague has called these "visual experiments." The primary problems with this approach concern how the model's parameters are varied (e.g. recognition of parameter correlations recognized and definition of the parametric ranges), and the abilities of the model to incorporate all of the important physical aspects (e.g. residual stresses, material nonlinearity). The use of analytical models introduces additional uncertainties and these additional uncertainties should not be omitted. In one recent case, the analytical models have been calibrated based on machined pipeline test sample results. Thus, the analytical models have 'carried over' the inherent Bias incorporated into the physical laboratory tests.

In this study, a differentiation has been made between physical laboratory test data and analytical test data. Further, differentiation has been made between physical laboratory test data on specimens from the field and those that are machined or involve simulated damage and defects. Earlier studies performed on these databases have clearly indicated potentially important differences between physical and analytical test data based Biases and differences between 'natural' and simulated defects and damage.

Burst Capacities of Corroded Pipelines

A test database consisting of 151 burst pressure tests on corroded pipelines was assembled from tests performed by the American Gas Association [2], NOVA [3], British Gas [4], and the University of Waterloo [5]. The Pipeline Research Committee of the American Gas Association published a report on the research to reduce the excessive conservatism of the B31G criterion (Kiefner, et al, 1989)[2] Eightysix (86) test data were included in the AGA test data. The first 47 tests were used to develop the B31G criterion, and were full scale tests conducted at Battelle Memorial Institute. The other 39 tests were also full scale and were tests on pipe sections removed from service and containing real corrosion.

Two series of burst tests of large diameter pipelines were conducted by NOVA during 1986 and 1988 to investigate the applicability of the B31G criterion to long longitudinal corrosion defects and long spiral corrosion defects [3]. These pipes were made of grade 414 (X60) steel with an outside diameter of 4064 mm and a wall thickness of 50.8 mm. Longitudinal and spiral corrosion defects were simulated with machined grooves on the outside of the pipe. The first series of tests, a total of 13 pipes, were burst. The simulated corrosion defects were 203 mm wide and 20.3 mm deep producing a width to thickness ratio (W/t) of 4 and a depth to thickness ratio (d/t) of 0.4. Various lengths and orientations of the grooves were studied. Angles of 20, 30, 45 and 90 degrees from the circumferential direction, referred to as the spiral angle, were used. In some tests, two adjacent grooves were used to indicate interaction effects. The second series of tests, a total of seven pipes, were burst. The defect geometries tested were longitudinal defects, circumferential defects, and corrosion patches of varying W/t and d/t. A corrosion patch refers to a region where the corrosion covers a relatively large area of pipe and the longitudinal and circumferential dimensions were comparable. In some of the pipes, two defects of different sizes were introduced and kept far enough apart to eliminate any interaction.

Hopkins and Jones (1992) [4] conducted five vessel burst tests and four pipe ring tests. The pipe diameter were 508 mm. The wall thickness was 102 mm. The pipe was made of X52. The defect depth was 40% of the wall thickness. Jones et al (1992) also conducted nine pressurized ring tests. Seven of the nine were machined internally over 20% of the circumference, the reduced wall thickness simulating smooth corrosion. All specimens were cut from a single pipe of Grade API 5L X60 with the diameter of 914 mm and wall thickness of 22 mm.

As part of a research project performed at the University of Waterloo, 13 burst tests of pipes containing internal corrosion pits were reported by Chouchaoui, et al [5]. In addition, Chouchaoui et al reported the 8 burst tests of pipes containing circumferentially aligned pits and the 8 burst tests of pipes containing longitudinally aligned pits.

The laboratory test database was used to determine the Bias in the DNV RP F-101 [6], B31G [7], and RAM PIPE [8] formulations were used to determine the burst pressure bias (measured burst pressure divided by predicted burst pressure). The results for the 151 physical tests are summarized in Fig. 10 and Fig. 11. These tests included specimens that had corrosion depth to thickness ratios in the range of 0 to 1 (Fig. 11). The statistical results from the data summarized in Fig. 10 are summarized in Table 1.

Table 1: Bias statistics for three burst pressure formulations (d/t = 0 to 1)

Formulation	B mean	B_{50}	V_B %
DNV 99	1.46	1.22	56
B 31 G	1.71	1.48	54
RAM PIPE	1.01	1.03	22

The RAM PIPE formulation has the median Bias closest to unity and the lowest COV of the Bias. The DNV formulation has a lower Bias than B31G, but the COV of the Bias is about the same as for B31G. The B31G mean Bias and COV in Table 1 compares with values of 1.74 and 54 %, respectively, found by Bai, et al [9]. The burst pressure test data were reanalyzed to include only those tests for d/t = 0.3 to 0.8. The bias statistics were relatively insensitive to this partitioning of the data.

A last step in the analysis of the physical test database was to analyze the Bias statistics based on only naturally corroded specimens. The results are summarized in Fig. 12 and Table 2. The Bias statistics for the DNV and B31G formulations were affected substantially. The results indicate that the machined specimens develop lower burst pressures than their naturally corroded counterparts. Even though the feature depth and area might be the same for machined and natural features, the differences caused by the stress concentrations, residual stresses, and metallurgical effects cause important differences.

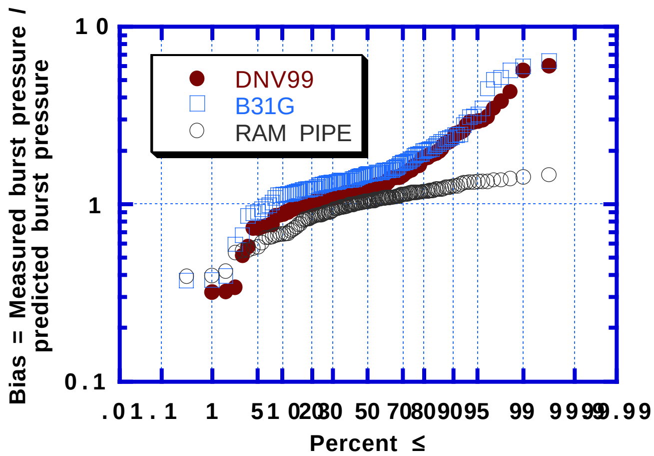

Fig. 10: Bias in burst pressure formulations (Lognormal probability scales)

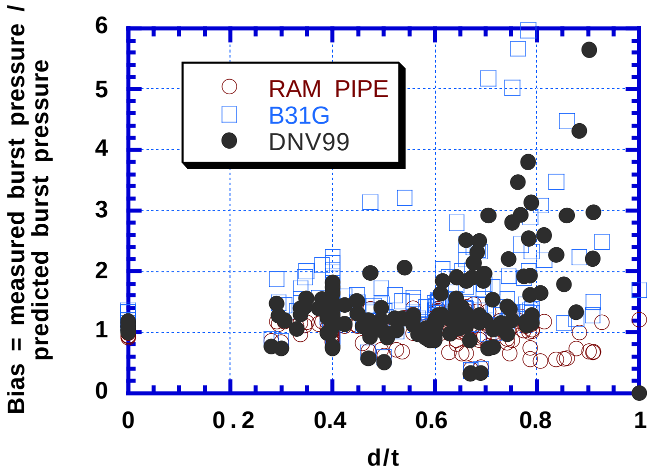

Fig. 11. Bias in burst pressure formulations as function of corrosion depth to wall thickness ratio (d/t)

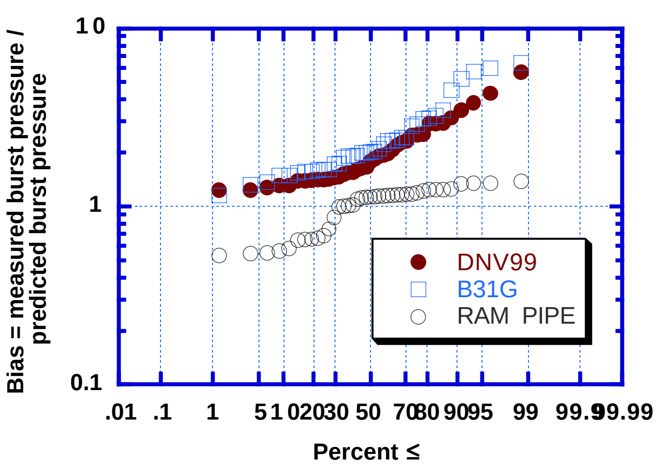

Fig. 12: Bias in burst pressure formulations for naturally corroded test specimens (Lognormal probability scales)

Table 2. Bias statistics for three burst pressure formulations – naturally corroded tests

Formulation	B mean	B_{50}	V_B%
DNV 99	2.10	1..83	46
B 31 G	2.51	2.01	52
RAM PIPE	1.00	1.10	26

Burst Capacities of Dented & Gouged Pipelines

A database on dented and gouged pipeline tests consisting of 121 tests was assembled from test data published by Battelle Research Corp. and British Gas [10-16] This database was organized by the sequence of denting and gouging and type of test performed. Study of this test data lead to the following observations:

- Plain denting with smooth shoulders has no significant effect on burst pressures. Smooth shoulder denting is not accompanied by macro or microcracking and the dent is re-formed under increasing internal pressures.
- Denting with sharp shoulders can cause macro and micro cracking which can have some effects on burst pressures and on fatigue life (if there are significant sources of cyclic pressures – straining. The degree of macro and micro cracking will be a function of the depth of gouging. Generally, given pressure formed gouging, there will be distortion of the metal and cracking below the primary gouge that is about one half of the depth of the primary gouge.
- Gouging can cause macro and micro cracking in addition to the visible gouging and these can have significant effects on burst pressures. In laboratory tests, frequently gouging has been simulated by cutting grooves in the pipe. These grooves can be expected to have less macro and micro cracking beneath the test gouge feature.
- The combination of gouging and denting can have very significant effects on burst pressures. The effects of combined gouging and denting is very dependent on the history of how the gouging and denting have been developed. Different combinations have been used in developing laboratory data. In some cases, the pipe is gouged, dented, and pressured to failure. In other cases, the pipe is dented and gouged simultaneously, and then pressured to failure. In a few cases, the pipe is gouged, pressured, and then dented until the pipeline looses containment. These different histories of denting and gouging have important effects on the propagation of macro and micro cracks developed during the gouging and denting. It will be very difficult for a single formulation to be able to adequately address all of the possible combinations of histories and types of gouging and denting.
- Gouging is normally accompanied by denting a pipeline under pressure. If the pipeline does not loose containment, the reassessment issue is one of determining what the reliability of the pipeline segment is given the observed denting and gouging. Addressing this problem requires an understanding of how the pipeline would be expected to perform under increasing pressure demands (loss of containment due to pressure) or under continuing

cyclic strains (introduced by external or internal sources). In the case of loss of containment due to pressure, the dent is re-formed under the increasing pressure and the gouge is propagated during the re-forming. Cracks developed on the shoulders of the dents can also be expected to propagate during the re-forming.

The analyses of the laboratory test database on the loss of containment pressure of dented and gouged pipelines was based on:

$$Pbd = (2\ SMTS\ /\ SCF_{DG})\ (t\ /\ D)$$

where SCF H_{DG} is the Stress Concentration Factor for the combined dent and gouge. Two methods were to evaluate the SCF associated with gouging and denting. The first method (Method 1) was based on separate SCF for the gouging and the dent reformation propagation:

$$SCF_G = (1 - d/t)^{-1}$$

$$SCF_D = 1 + 0.2\ (H/t)^3$$

$$SCF_{DG} = [(1 - d/t)^{-1}]\ [1 + 0.2\ (H/t)^3]$$

The second method (Method 2) was based on a single SCF that incorporated the gouge formation and propagation:

$$SCF_{DG} = \{[1 - (d/t) - [16\ H/D(1-d/t)]\}^{-1}$$

Fig. 13 summarizes results from analysis of the test database. The dent depths (H) to diameter ratios were in the range H/D = 1.0 % to 3.6 %. The gouge defects had depths (h) to wall thickness ratios that were h/t = 25%.

Results of the analyses indicate Method 1 has a median Bias of B_{50} = 1.2 and a COV of the Bias of V_B = 33%. Method 2 has a B_{50} = 1.3 and V_B = 25%.

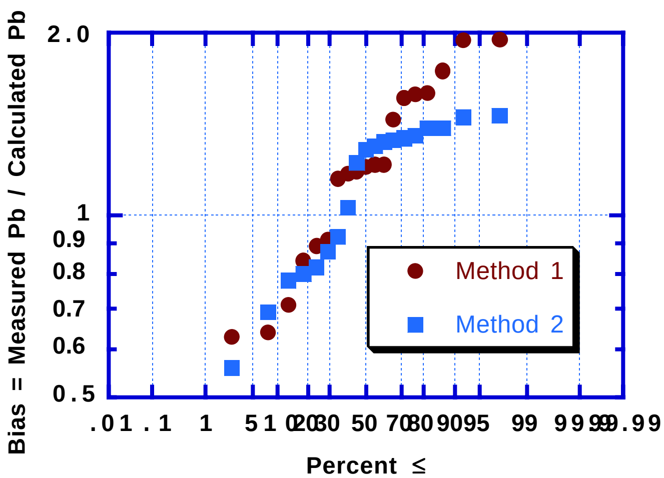

Fig. 13: Analysis of test database on pipelines with dents and gouges

SYSTEMS AND SEGMENTS

In development of the formulation for the probability of failure, it is important to discriminate between pipeline 'segments' and 'systems'. A pipeline system can be decomposed into sub-systems of a series segments. A series segment is one in which the failure of one of the segments leads to the failure of the system.

A series (weak-link) system fails when any single element fails. In probabilistic terms, the probability of failure of a series system can be expressed in terms of the unions (∪) of the probabilities of failure of its N elements as [17]:

$$Pf_{system} = (\ Pf_1\ ) \cup (\ Pf_2\ ) \cup \ldots (\ Pf_N\ )$$

For a series system comprised of N elements, if the elements have the same strengths and the failures of the elements are independent (ρ = 0), then the probability of failure of the system can be expressed as:

$$Pf_{system} = 1 - (1 - Pf_i\ )^N$$

If Pfi is small, as is usual, then approximately:

$$Pf_{system} \approx N\ Pf_i$$

If the N segments of the pipeline are independent and have different failure probabilities:

$$Pf_{system} = 1 - \prod_{i=1}^{N} (1 - Pf_i)$$

If the segments are perfectly correlated then:

$$Pf_{system} = \text{maximum}\ (Pf_i)$$

There can be a variety of ways in which correlations can be developed in elements and between the segments that comprise a pipeline system. Important sources of correlations include:

- segment to segment strength characteristics correlations, and
- segment to segment failure mode correlations.

The correlation coefficient, ρ, expresses how strongly the magnitudes of two paired variables, X and Y, are related to each other. The correlation coefficient ranges between positive and negative unity (-1 ≤ ρ ≤ +1). If ρ = 1, they are perfectly correlated, so that knowing X allows one to make perfect predictions of Y. If ρ = 0, they have no correlation, or are 'independent,' so that the occurrence of X has no affect on the occurrence of Y and the magnitude of X is not related to the magnitude of Y. Independent random variables are uncorrelated, but uncorrelated random variables (magnitudes not related) are not in general independent (their occurrences can be related) [17].

Frequently, the correlation coefficient can be quickly and accurately estimated by plotting the variables on a scattergram that shows the results of measurements or analyses of the magnitudes of the two variables. Two strongly positively correlated variables will plot with data points that closely lie along a line that indicates as one variable increases the other variable increases. Two strongly negatively correlated variables will plot with data points that closely lie along a line that indicates as one variable increases, the other variable decreases. If the plot does not indicate any systematic variation in the variables, the general conclusion is that the correlation is very low or close to zero.

In general, samples of paired pipeline segments are strongly positively correlated; tensile strengths, collapse pressures, and burst pressures show very high degrees of correlation (Figs. 14-16) [18]. These test data were taken from samples of delivered pipeline joints and were not intentionally paired from the same plate or runs of steel. High degrees of correlation of pipe properties were also found by Jaio, et al (1997) for samples of the same pipe steel plate.

These results have important implications regarding the relationship between the reliability of a pipeline system and the reliability of the pipeline system elements and segments. The probability of failure of the pipeline system will be characterized by the probability of failure of the most likely to fail element – segment that comprises the system.

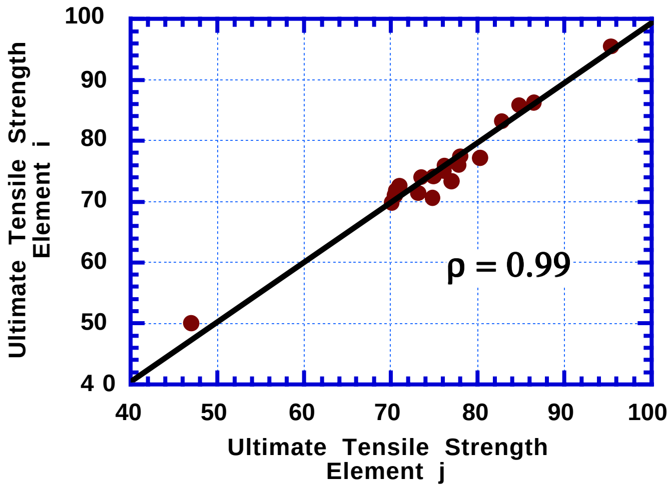

Fig. 14: Correlation of measured ultimate tensile strengths of paired pipeline steel samples from adjacent pipeline segments

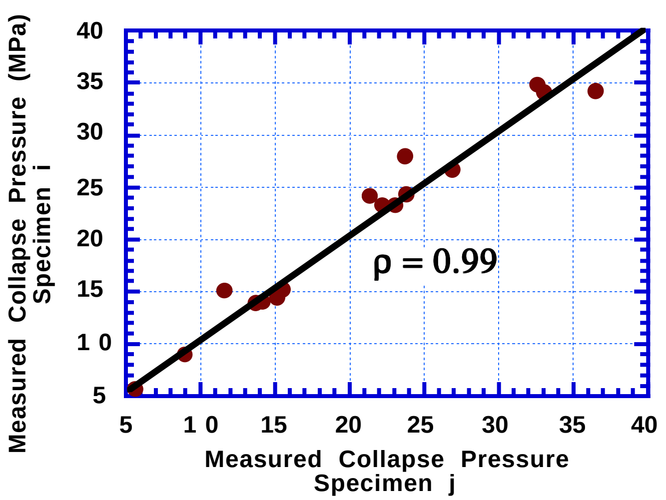

Fig. 15: Correlation of measured collapse strengths of paired steel pipeline samples from adjacent pipeline segments

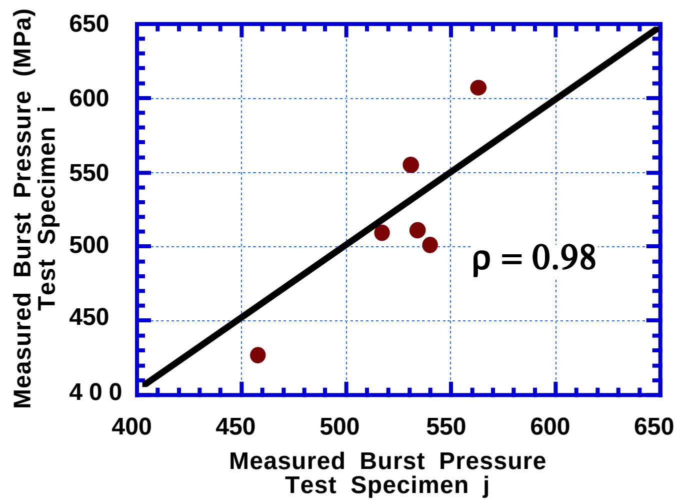

Fig. 16: Correlation of measured burst strengths of paired steel pipeline samples from adjacent pipeline segments

Correlations can also be developed between the failure modes. A useful expression to determine the approximate correlation coefficient between the probabilities of failure of a system's components (or correlation of failure modes) is:

$$\rho_{fm} \approx \frac{V_S^2}{V_R^2 + V_S^2}$$

where V^2_S and V^2_R are the squared coefficients of variation of the demand (S) and capacity (R), respectively. It is often the case for pipeline systems that the coefficients of variation of the demands are equal to or larger than those of the capacity. Thus, the correlation of the probabilities of the failure of the system's segments can be very large, and there is a high degree of correlation between the system's failure modes. Again, this indicates that the probability of failure of the system can be determined by the probability of failure of the system's most likely to fail segment.

CONCLUSIONS

A practical formulation has been developed to allow 'real-time' assessments of pipeline likelihoods of LOC (probabilities of failure). This development as involved developing analytical models to evaluate time effects, Biases introduced by different models used to evaluate the LOC pressures, and system versus segment probabilities of failure. Laboratory test data has been used to provide the important parameters for these analytical models.

The real-time RAM formulation is a Level 2 approach in the general pipeline Inspection, Maintenance, and Repair process proposed by Bea, et al [19]. This formulation is consistent with the Risk Based Inspection process proposed by Bjornoy, et al [20]. Verification of the real-time RAM LOC analytical models with field hydro-test to failure data is the subject of a companion paper [21].

The ability to develop real-time estimates of the probabilities of LOC can provide the pipeline owner / operator, pipeline engineers, and regulators with useful additional information to help guide their decisions regarding pipeline maintenance.

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