Intelligence Tools for Environmental Threats: Integrated Technologies for Chemical Hazards

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ABSTRACT

Accounting for environmental hazards in mission planning requires the most up-to-date observations and forecasting of the dynamic battlefield environment. In addition, some hazards, such as the exposure to toxic industrial chemicals and materials (TIC/Ms) in complex urban environments, cannot be predicted in time and space without significant a priori knowledge of TIC/Ms presence in the battlefield, potential release scenarios, and the dynamic ongoing natural environmental processes that result in hazardous soil, water, and air exposures. Teams at the US Army Engineer Research and Development Center (ERDC) are engaged in the development of tools to improve the timeliness and reduce the uncertainty of TIC/Ms risk identification through the integration of spatial and database tools including probable TIC/M locations and quantities, toxicological hazards, fate and transport properties, and soil properties. Furthermore, ongoing efforts to expand the reach of operational hydro-meteorological prediction allow these tools to be applied in rapid fate and transport modelling with greater certainty over a larger swath of the globe than is presently possible. The end result will enable more accurate and dynamic understanding of the chemical hazard potentials that can be encountered during battlefield operations, allowing for better informed routing and equipment selection.

1.0 INTRODUCTION

The presence of toxic industrial chemicals and toxic industrial materials (TIC/Ms) in contested areas creates a challenge for accurately assessing and planning for Warfighters' exposure risks. Chemical hazards encountered during operations may come from a variety of sources, including purposeful releases of a predictable scale such as chemical and biological weapon strikes, purposeful releases of improvised chemical weapons, or purposeful and accidental releases of chemical materials stored or transported in and around areas of operation. Therefore, Warfighters generally lack the understanding of potential lethal environments that may be encountered during active engagement and predictions of how to operate in, avoid, or prepare for exposure during sustained operations.

1.1 Need for this capability

There are several existing utilities, tools, and models used to inform planning practices on chemical hazards and risks. This includes several web-based software applications such as the Joint Acquisition CBRN Knowledge System (JACKS), Joint Warning and Reporting Network (JWARN) the early warning system, and the Joint Effects Model (JEM) and CBRN-Information Systems (CBRN-IS) that report hazards and suspected impacts. These programs rely on a number of individual media modelling capabilities including HPAC for aerial dispersion modelling, Incident Command for Drinking Water Protection (ICWater) and Specialized Hazard Assessment Response Capability (SHARC) for waterborne hazard modelling, and others. The US Army needs intelligence tools that will predict, quantify, and plan for TIC/M potential threat and these tools need to enable a near real-time dynamic ability to identify and assess chemical threats.

1.2 Integrated project objectives

This effort seeks to improve mission planning and situational awareness by predicting TIC/M threats on timescales relevant for mission planning through integrated chemical hazard modelling. This solution must include:

- Mechanistic, quantitative models for rapid chemical environment evaluation and intuitive impact assessments to support mission planning, situational awareness, and mission success
- Knowledge of industries' potential chemicals, including transport profiles, interaction and degradation (air, water, soil) in dynamic operating environments
- Breakdown products of chemical agents of opportunity

2.0 SURVEILLANCE OF TIC/MS

2.1 TIC/Ms Surveillance gap

Due to the vast diversity of TIC/Ms, the US Army relies on multiple databases of chemical information as TIC/M resources during mission planning. These databases, for example those used in the JEM program, are extensive, but are not complete of all TIC/Ms, some of which present a significant exposure risk to the Warfighter. Additionally, the JEM program does not include the potential threats due to chemical breakdown products created in the environment after release, and the complete chemical properties for many breakdown products are not present in chemical property databases. Thus there is need to create tools that can identify and quantify TIC/Ms and their breakdown products based on identified industries.

2.2 TIC/M Intelligence database solution

The TICM-DB tool (Figure 1) is designed to field a variety of potential queries such as TIC/Ms associated with particular industries, potential TIC/Ms from illicit activities, and additional chemical breakdown products potentially resulting from deliberate fires and collateral damages. As shown in Figure 1, this is achieved by bringing together multiple sources of information.

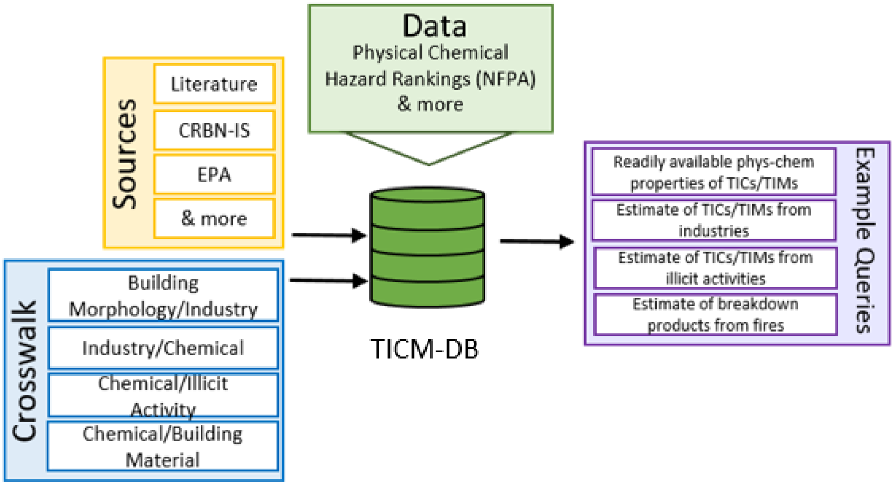

Figure 1, TICM-DB product

The ability to estimate the presence of TIC/M compounds in urban and industrial battlefields is necessary to identify potential sources of chemical hazards. A survey of the US Environmental Protection Agency (EPA) Toxic Release Inventory (TRI) has previously been used to develop relationships between particular industries with the types of chemicals that are used in those industries [1]. The TRI reports on annual releases from industrial and civic chemical use sites such as those operated in the manufacturing, service, and transportation industries. While the TRI gives detailed information about activities within the US, the relationships between certain industries and certain chemicals are broadly applicable. Further development of this capability is based on the hypothesis that most industrial sites throughout the world are based on US, European, Russian, Japanese, Korean, or Chinese design allowing the development of a library of industries based on site morphology. When combined with the identification of an area of interest (AOI) from socio-political mapping sources and other data, the relationships between industries and chemicals become a powerful TIC/Industry crosswalk capability (Figure 2) for estimating the potential for chemical threats where ground level intel is sparse.

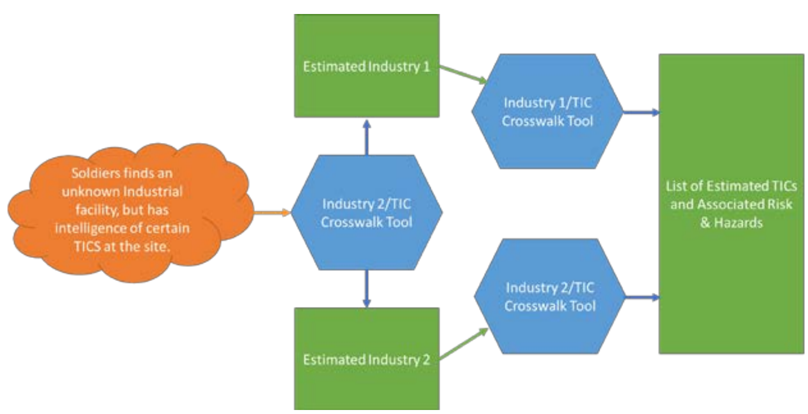

Figure 2, TIC/Industry crosswalk tool to develop chemical site risk information from limited knowledge

The TICM-DB tools also incorporate unconventional sources of TIC/M related hazards. Chemicals not traditionally identified with weaponry may also present incidental release or improvised weapons hazards due to their chemical and toxicological properties. Other materials in the contested environment such as building materials may release hazardous compounds if burned. Illicit drug manufacturing and processing activities constitute an industrial activity outside the purview of the TRI. Web scraping techniques are being utilized to develop data sets of observable and quantifiable georeferenced information to serve as the basis of relationships that predict the type and quantity of unconventional materials in AOIs. TICM-DB is also being designed for flexible expansion to include other hazardous materials that are not considered TICs such as radioisotopes, flammable, and reactive materials.

A second critical component, the quantities of TIC/Ms in an AOI, is needed for any estimate of the potential exposure. Cross walking the presence of industries and the associated chemicals that may be present with the chemical volume or masses needed to support production levels establishes de minimus TIC/Ms quantities in the AOI. Further refinement is enabled by site specific morphology such as visible presence or absence of storage tanks, observed production rates, reported profits, and other financial information. Real-time updating can be informed by observations of delivery, product, and waste transportation.

3.0 CHEMICAL PROPERTIES

3.1 Chemical property need

Even for known weaponized and improvised chemical threats, the physical chemical properties aspects of the current databases are incomplete. This is partially due to the vast nature of possible chemicals that may be encountered, the lag in testing to establish new materials, and the limited requirements in many countries for required reporting of proprietary formulations.

3.2 Chemical property solution

Working on the hypothesis that better quality TIC/M data is achievable, missing properties are being identified and values provided by multiple methods. Some of the desired data for all chemical species of interest are density, viscosity, solubility, pKa, Henry's law constant, vapor pressure, free energy of solvation, boiling point, flash point, partitioning coefficients (K_{ow}, $K_{heptane\text{-}water}$, K_{oc}), Micelle/membrane interactions, degradation kinetics, and potential impact on soldiers, which might be detrimental to potential operations in the contested environment. Efficient computational algorithms (Figure 3) are used for the gap analysis of existing property data in which data is sourced from existing databases, literature, and web sites and gaps are identified and tabulated. The algorithm examines the range of parameter values and the dependency of chemical property parameters on other variable parameters as an assessment of existing chemical property data quality and uncertainty.

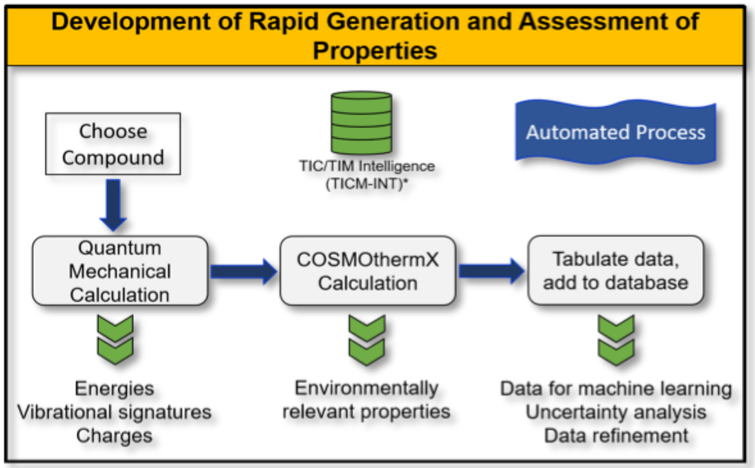

Figure 3, Automated process for the completion of TIC/M database information.

Computational chemistry allows the synthetic generation of chemical property data based on quantum-chemical first principles in a statistical thermodynamic framework. The obtained values will be compared with the data obtained at other computational levels such as by Estimation Program Interface v4.11 (EPI SuiteTM), which is a QSAR based predictive package distributed by US EPA and, for those compounds with identified experimental values, compared against measured values. Those data with significant disagreement will be further analysed and will be computed using more rigorous calculations using ab initio and molecular dynamics simulation approaches and thus uncertainty in the data will be minimized. For those compounds with incomplete experimental data sets and for new compounds without experimental data the computational method provides predictive capabilities to fill the gaps in the chemical property database thereby improving and expanding the capability to predict exposure risk to the Warfighter. The resulting chemical property database for the fate, transport, and effects of compounds in complex media will be linked to a database of degradation kinetics for compounds in the natural environment.

3.2.1 Chemical reactivity mapping

There is no product currently available in the field that rapidly predicts exposure risk due to the chemical products of reaction and degradation in the environment. That capability first requires the prediction of viable reaction pathways. A recently developed semi-empirical method computationally generates multistep chemical reaction pathways from the very first step (reagents) to final product including intermediate and speed limited steps. Kinetic parameters are computed from Gibbs free energy changes over a range of temperatures. The speed of reagent decay and product formation can be predicted along with half-lives of key components using the computed kinetic parameters. Reaction kinetics with selected reactive species available in natural surroundings as well as bulk water will also be evaluated for selected compounds.

3.2.2 Phase partitioning

Phase partitioning properties are necessary to asses TIC/M transport in the complex multimedia environment. Of particular concern are mass partitioning from liquid phase release to gas phase and liquid or gas phase release to solid surfaces. In the first case this is because chemicals in the gas phase typically migrate more rapidly from the release point and in the latter case it is because some chemicals may present a long lasting residual exposure hazard in surface soils and the built environment. Electronic structure calculations are planned to compute several partitioning coefficients such as K_{ow}, $K_{heptane\text{-}water}$, K_{oc}, Micelle/membrane interactions using the Gaussian 09, Turbomol, and COSMOmic software packages. Select properties will also be computed using traditional density functional theory and molecular dynamics simulation approaches.

3.2.3 Data analysis/quality assurance

Computational algorithms will be developed to expedite computational data generation using various computational chemistry methods for efficient data analysis and uncertainty reduction among the data already available from the literature. Calculation of correlation coefficients will help to understand the prediction reliability of computational data as well as the quality of the experimental data. Data with greater uncertainty will undergo further analysis and more rigorous calculation to refine the predicted physical and chemical properties. These methods also allow the generation of temperature dependent properties which facilitates high fidelity fate and transport modelling across a wider range of local conditions.

4.0 FATE AND TRANSPORT

4.1 Dynamic Fate and Transport need

Warfighters interacting with water bodies during and after TIC/M release events need actionable information about contaminant exposure risk. Chemicals released to water bodies result in spatially and temporally dynamic concentrations that expand and flow downstream over time. In addition, contaminants are frequently present even when they are not visible and may create a secondary hazard by volatizing to the air around the stream both of which increase the risk in using in-situ visual inspection as a mechanism to assess exposure potential.

4.2 Fate and transport solution

Georeferenced modelling tools can rapidly identify TIC/M exposure risk in an actionable format. The desired product informs on the extent of chemical spread and the severity of the contamination in terms of hazard risk in a time dynamic presentation. The development of a singular site model for a defined temporal period is not a novel capability but expansion to a non-site specified and dynamic utility that can be applied to multiple sites without knowledge of the chemical compounds a priori requires additional inputs as automated data streams rather than user formatted files (Figure 4).

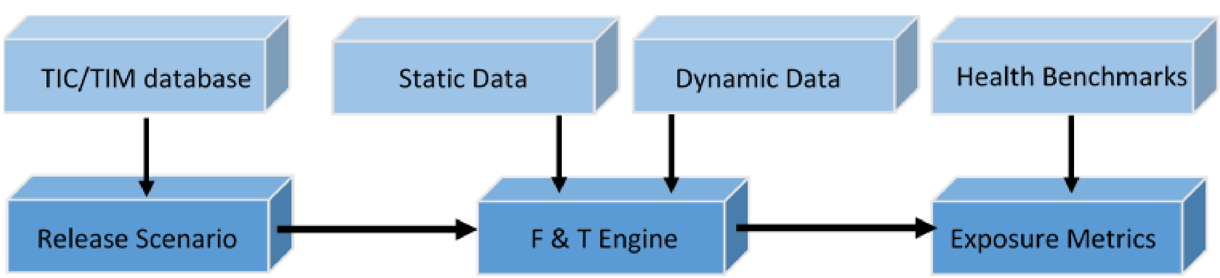

Figure 4, Essential components of the ITCH model system to predict dynamic human exposure

4.4.1 Release scenarios designed for minimal user input

The TICM-INT tools being developed to identify potential sources and quantities of chemicals within a contested AOI are critical for determining potential concentrations in surface water due to chemical releases. Similarly, much of the static description of the AOI can be extracted from georeferenced datasets such as drainage areas, infrastructure and stream channel locations, and soil types (as informed by the pedoinformatic approach described previously). But, for dynamic modelling, the rate of release is also a critical component. The models for rapid surface water concentration currently available require extensive user input to characterize chemical sources, failure, and release mechanisms because the rate that mass enters the environment to initiate exposure is calculated from detailed physics based scenarios. In the ITCH fate and transport system a guided decision tree approach is being developed that incorporates key information about the range of parameters used for the detailed physics based scenarios. In addition, the system will identify greatest risk scenarios that assume the maximum release rate anticipated for a given type and volume of storage to provide users an upper limit of exposure as well as an expected value or chemical concentration.

4.2.2 Dynamic system of data and models

A second key component of our approach is the inclusion of near real-time and forecasted dynamic data to describe the hydro-meteorological conditions of the AOI. Although average annual properties such as temperature, precipitation, streamflow, wind speed, and wind direction can be used to produce acceptable estimates of the long term average expected behaviour of a system, that is not be sufficient to predict the potential exposure for a specific ongoing or near future activity due to the high variability of the hydro-meteorological parameters. Authoritative global meteorological data is linked to ERDCs Streamflow Prediction Tool which performs hydrologic and mass routing. An uncoupled one dimensional advection dispersion model moves the chemical hazard downstream, allowing it to spread over time resulting in concentration time series for each stream reach in the AOI. The advection dispersion model also adjusts the quantity of contaminant in the water column based on solid sorption in the water column and to sediment, partitioning to the gas phase, and degradation kinetics.

4.2.3 Visual Display of Actionable Information

Figure 5 demonstrates the anticipated surface water chemical hazard mapping product. Figure 5(a)shows the concentration time series at a single stream segment location informed by the chemical release scenario, dynamic hydrologic routing, fate determining processes. Comparison between the modelled concentrations and benchmark health effect screening concentrations results in an assignment of risk levels. Figure 5(b) shows the result of multiple stream reach concentration and benchmark comparisons for single time. This type of output could be used to determine gap crossing locations with reduced exposure risk.

a. **b.**

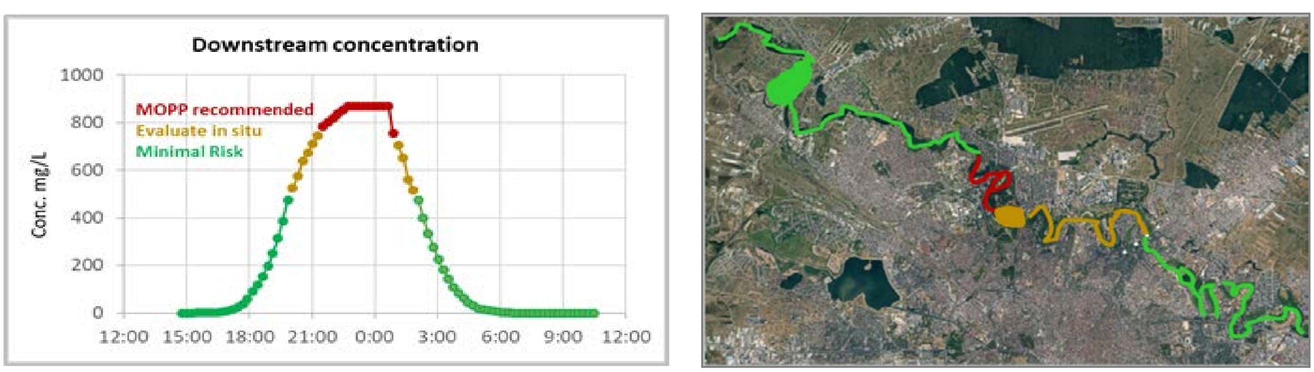

Figure 5, actionable display of chemical hazard in stream

5.0 SOILS

5.1 Soil need

There is a high likeliness that Warfighters will interact with contaminated soils during and after a TIC/M event that is not accounted for in mission planning. Furthermore, exposure via soil contact is not currently modelled as a dynamic source of risk to the Warfighter. But of all the media, soil can be transported with the Warfighter and has the capability to lead to longer exposure durations and therefore higher risk. This can result in significant negative consequences for mission success. The complexity of soils represents a formidable technology barrier in predicting contaminant environmental fate. Complexity arises from the fact that soils are both chemically and physically heterogeneous multiphase materials that respond dynamically to the biological and hydro-meteorological surroundings while reflecting the geologic history of their locale. In addition, human activities can change the chemical and physical behaviour of soils, directly impacting contaminant fate. Urban soils, and those taxonomically indentified as anthrosols and/or technosols, are unique and complex materials that can be considered physically and chemically disturbed from their pristine state. The fate and transport of chemical hazards to groundwater, surface water, and the atmosphere in contested urban environments depends on accurate characterization and mapping of urban soils and their expected properties.

5.2 Soil solution

Increased mission readiness and situational awareness can be enabled by understanding TIC/Ms fate and transport in soils, including urban soils. Thus there is a need to identify, classify, and characterize urban soils with similar geomorphological factors globally, and quantify sorption/degradation parameters in these urban soils of selected TIC/Ms.

5.2.1 Development of urban soil analogs

A field collection protocol [2] hat is applicable to urban soils will be applied to collect samples at location analogs for AOIs outside the United States. In the urban environment, ongoing soil formation processes combined with the pre-existing pristine soil properties create the unique properties of the anthrosol. Features such as abrupt and clear depositional boundaries, specific and strong chemical features (i.e. stark pH or mineralogy contrast), altered physical features, specific biologic (flora and/or fauna) communities, early stage pedogenesis, or synlithogenesis are specific soil forming factors that can be used to classify an anthrosol. The selection of analog sites is non-trivial requiring the application of a pedoinformatic approach that accounts for factors such as USDA-NRCS and/or WRB classification, parent material, climate, landscape position, and vegetation. Field collections extend to a depth of 24" from the soil surface. A thorough physico-chemical characterization generates base data for a multivariate geo-statistical analysis to determine which of the soil physicochemical factors are tied to chemical fate.

5.2.2 Experimental sorption/degradation of TIC/Ms in urban soils

Multiple processes affect the fate and transport of hazardous chemicals in urban soils including sorption, degradation, and surface complexation. As urban soils are characterized a selection of representative surfaces will be selected for additional studies utilizing microcosm and breakthrough column approaches to evaluate the role of urban soil constituents on chemical retention and the ultimate potential for chemical exposure. Soil constituent factors such as silicates, carbonates, metal oxides, and organic material are likely to be important factors. Soil specific chemical parameters established through batch isotherm and kinetic studies will also serve as validation experiments for the previously described computational prediction of sorption and reaction parameters.

5.2.3 Digital soil mapping

Chemical and physical soil heterogeneity leads to a heterogeneous fate and transport behaviour in the environment. To utilize the chemical fate parameters determined for urban soils there needs to be a georeferenced capability to identify the soil in the AOI, the heterogeneity of that soil, and the associated physical chemical properties to apply. Digital map layers will enable the linkage between location and appropriate properties which in turn informs which fate determining processes are significant at a given site. This reduces the burden to individually generate fate and transport models for specific locations and increases the fidelity of the model to the range of observed or modelled system properties. The result is an improved prediction of the potential for exposure via soil transference in contested areas.

6.0 PLANNED INTEROPERABILITY WITH OTHER CAPABILITIES

6.1 USACE DRiVE package

Course forecasting, navigation, and routing tools need to account for the fixed physical environment as well as short term changes in conditions. These conditions can include traffic, weather, road hazards, human movement, and other difficult to predict influences on the safety and suitability of a particular course. A real-time analysis of the visual field can provide moment-by-moment information on some of the dynamic conditions, but no tools are currently available that manage exposure risks from the chemical hazards present in contested environments. Given that exposure pathways along soldier routes present a risk for adverse effects that may include physical and/or mental impairment, there is need for a product that can proactively manage exposure risk by assessing the potential for exposure and presenting alternative routing options.

6.2 Drive overview solution

ERDC is developing routing tools that incorporate the products described for the ITCH project above in the DRiVE package. The DRiVE project also incorporates airborne chemical hazards generated from a separate modelling effort but dependent on the same TICM-DB databases and computationally derived chemical properties as the ITCH project. A Toxicological Operational Knowledgebase System (TOKS) is planned to expand on the TICM-DB database with biological effects of TIC/Ms and conventional chemical, biological, radiological and nuclear threats. Multiple acute inhalation toxicity reference values will be leveraged to develop probabilistic assessments of risk. Routing decisions in DRiVE utilize probabilistic risk and cost function game theory rather than shortest travel distance or travel duration to choose acceptable routes. Thus, risk due to multiple sources can be accommodated in route selection.

7.0 CONCLUSIONS

7.1 Implications of this work

Future mission planners will have increased capability through the ITCH tools to assess potential lethal environments that may be encountered during active engagement. Sparse ground level data on the location and quantity of TIC/Ms in the urban environment will no longer limit the ability accurately assess chemical hazard exposure risks. Utilizing advanced computational methods to determine the properties that govern the fate of chemicals in the environment, higher fidelity modelling will be available for a comprehensive list of chemicals and chemical breakdown products. With near real-time capability to ingest and process hydro-meteorological conditions and the ability to predict soil properties in urban environments the dynamic fate and transport of TIC/Ms win surface water and soils will also be predictable. This will reduce the risk of impaired soldier functions or mortality due to unplanned exposures and increase tactical advantages during operation and sustainment in contested urban environments.

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