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Residues at Clandestine Methamphetamine Laboratories and Their Health Effects

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ABSTRACT: There has been a sharp increase in the existence of methamphetamine related clandestine laboratories in Malaysia. When a clandestine laboratory is discovered, the law enforcement personnel normally remove the bulk of the chemicals. However, contamination remaining in the structure (ranging from visible stains to invisible residues) is still a concern. It is therefore important to identify the chemicals that could have been present, used and/or generated in a clandestine laboratory, and the health risks posed by them to law enforcement personnel as well as the future occupants of the structure. This article reviews the scientific literature and reports on clandestine laboratories, with particular focus on the residues present at clandestine laboratory sites, and current knowledge of the health risk associated with these.

Keywords: clandestine laboratory, methamphetamine, residues, exposure, health

Introduction

A clandestine laboratory is a place where preparation of illegal substances occurs. It consists of a sufficient combination of apparatus and chemicals that can be or has been used in the manufacturing of the illegal substances (Christian, 2004). The term clandestine laboratory covers the manufacture of drugs, explosives, biological and/or chemical weapons, however, the most common clandestine laboratories encountered involve the manufacture of methamphetamine. Clandestine methamphetamine laboratories vary in size. The large and highly organised clandestine laboratories, sometimes termed "super labs" or "mega-labs", have high production capacity and are often run by skilled-operators, while smaller laboratories have the ability to produce much smaller amounts of methamphetamine during each production cycle (NDIC, 2001). The smaller laboratories may actually present a greater risk to the general population because they are normally operated by less-skilled operators (often the drug users) who have no or little chemistry background. Also, very often makeshift equipment and facilities are used and these pose high potential for fire and explosions. Uncontrolled and illegal waste disposal by these operators also result in serious structure contamination and environmental hazards.

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Clandestine laboratory situation in Malaysia

The number of clandestine laboratories, particularly those involving in methamphetamine manufacture, is on the rise in Malaysia (Reid and Costigan, 2002; UNDOC, 2008). Twenty-six amphetamine type substance laboratories were seized from 1997 to 2000 (Reid and Costigan, 2002). From 2004 to 2007, several methamphetamine mega-laboratories were dismantled (UNDOC, 2008). The country's first large capacity clandestine laboratory was dismantled in Semenyeh in 2004 (Chan, Sulaiman et al., 2009). This laboratory utilized the traditional Emde synthesis route favoured by Southeast Asian drug rings (Chan, Sulaiman et al., 2009). The laboratory dismantled in Kulim in 2007 contained several hundred kilograms of finished and semi-processed methamphetamine using the Phenol-2-propanone (P2P) method in which mercury chloride was used (Office of Drugs and Crime, 2007; Chan, Sulaiman et al., 2009). Another methamphetamine mega-laboratory was discovered in Senai, Johor in May 2008 (Vijayan, 2008). The number of clandestine laboratories actually operating may be greater than those numbers listed above. These laboratories have definitely posed a great danger to the first responders and general public particularly by their physical, chemical and environmental hazards.

Chemicals used in clandestine laboratories can be flammable, reactive, corrosive, and/or toxic. Toxic substances are also produced when the drugs are "cooked". As a result, the clandestine laboratory operators or "cooks", occupants, law enforcement personnel, neighbours, and future occupants of a clandestine laboratory can all be at risk from hazardous chemical exposure. The health risks posed from such exposure must be taken into account by all these parties, as well as the appropriate authorities.

Hazards of methamphetamine clandestine laboratories

The manufacturing process of methamphetamine presents many hazards, particularly during the production stage (Cameron, 2002). The production of methamphetamine requires the use of chemicals which may be flammable, corrosive, explosive and toxic(Auckland Regional Council, 2003). These chemicals pose chemical hazards when one comes into contact with them. Also, chemical by-products such as toxic phosphine gas may be released during some types of methamphetamine manufacture that could lead to fatalities (Russo, 1999). Adverse health effects in law enforcement personnel as a result of phosphine exposure from a methamphetamine laboratory investigation have been reported (Burgess, 2001). Fire or explosion may occur due to improper handling of chemicals, inappropriate makeshift apparatus, unexpected chemical interaction or processing errors(Minnesota Department of Health, 2004).

Very often, clandestine laboratory operators have little concern for public safety or the environment (Auckland Regional Council, 2003). They may dump toxic waste down kitchen sinks, toilets, stormwater, drains, and on the ground surrounding the laboratories or roadsides. It has been estimated that the production of methamphetamine leads to 5-6 times as much toxic waste on a per mass basis . The illegal disposal results in environmental contamination . Soil and water contamination occurs as the waste accumulates, and the public may be exposed to these corrosive, toxic and flammable hazards .

Structure and vehicle contamination can also occur as a result of methamphetamine production. The cooking process produces vapours which present immediate exposure hazards, and may also lead to long-term hazards for cooks and residents of the laboratory. Adverse effects from chemical exposure in clandestine laboratories have been reported (Burgess, Barnhart et al., 1996; Russo, 1999; Burgess, 2001; Burgess, Kovalchick et al., 2002; ONDCP, 2003).

Chemicals likely to be present in a clandestine laboratory

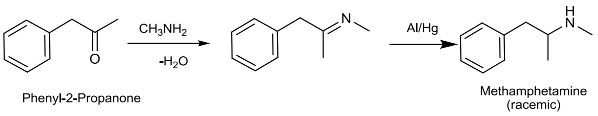
The chemicals used in a clandestine laboratory depend on the method used to synthesise methamphetamine. However, other chemicals not required in the actual manufacture of methamphetamine may also be present, possibly through theft from stores or chemical supply companies. Furthermore, there are hundreds of chemical products and substances which can be used interchangeably to produce methamphetamine (Minnesota Department of Health, 2004). Table 1 lists the chemicals used in a variety of methods to produce methamphetamine. Note that as the methods of production changes, the chemicals associated with this activity will also change. Chemicals commonly used in Malaysia (Office of Drugs and Crime, 2007) are bolded while those used in Red Phosphorus and Anhydrous Ammonia laboratories (common in the US) are marked with an asterisk. Note that most of them are readily-available materials since they have legal household or commercial uses.

Methods of manufacturing

There are many methods which can be used for the manufacture of methamphetamine, using one of several basic chemical processes. Allen *et. al.* (1989) reviewed reductive approaches to amphetamine and methamphetamine via heterogeneous catalysis, dissolving metals, metal hydrides and non-metal reductions (Allen and Cantrell, 1989). The most common methods reported in the Forensic Science literature are the Amalgam Method, the Red Phosphorus Method, and the Anhydrous Ammonia Method (Frank, 1983; Allen and Cantrell, 1989; Ely and McGrath, 1990).

The amalgam method

The Amalgam Method uses P2P and methylamine as the primary precursors. Note that the mega-laboratory seized in Kulim in 2006 utilised these precursors (Office of Drugs and Crime, 2007) . A common method of synthesis known as the "Mercuric Method" uses P2P, methylamine, mercuric chloride and aluminium metal in alcohol to synthesise methamphetamine (Frank, 1983; Irvine and Chin, 1991), as shown (Frank, 1983; Christian, 2004):



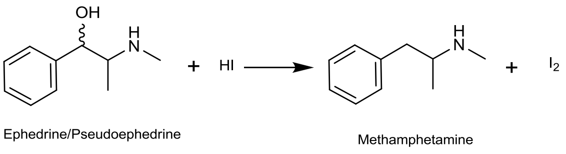
This method, however, became less common after P2P was categorised as a Schedule II controlled substance in 1980 in the US (Irvine and Chin, 1991). Nevertheless, many clandestine chemists began to synthesis their own P2P, for instance, from phenylacetic acid with acetic anhydride or lead acetate (Allen, Stevenson et al., 1992). The mercuric method potentially contaminates the final product with mercury if it is not adequately purified (Davidson, 1983; Irvine and Chin, 1991). However, no literature was found to reveal any cases of mercury poisoning from methamphetamine. Phenylacetic acid, a precursor for P2P synthesis, has a strong 'cat urine' smell which makes its handling easily detected (Irvine and Chin, 1991). Lead acetate can cause lead poisoning if present in the final product (CDC, 1990). The Amalgam Method has been reported to yield racemic methamphetamine of low quality(M S Scott; Rhodium, 2004).

TABLE 1- Chemicals used in a variety of methods to produce methamphetamine (Sources: CDPHE 2003; Minnesota Department of Health 2004; Illinois Department of Public Health 2005; Office of Drugs and Crime 2007)

- Acetaldehyde
- Acetic anhydride
- Acetone *
- Aluminium chloride
- **Aluminium metal**
- Anhydrous Ammonia *
- Ammonia
- Ammonium acetate
- Ammonium chloride
- Barium sulfate
- **Benzaldehyde**
- Benzene
- Benzyl chloride
- **Benzyl cyanide**
- Benzyl magnesium chloride
- Bicarbonate of soda
- n-butyl amine
- Butyl alcohol
- **Camphor oil**
- Carbon dioxide
- Chloro acetone
- Chloroform *
- Chloropseudoephedrine
- Cyclohexane
- Dry ice
- Ephedrine * (Cold tablets)
- **Ethyl acetate**
- **Ethyl alcohol**
- **Ethyl ether * (Engine starter)**
- **Ferric chloride**
- Formaldehyde
- Formic acid
- Freon
- Hexane
- Hydriodic acid *
- Hydrochloric acid *
- Hydrofluoric acid
- Hydrogen
- Hydrogen peroxide
- Hydrogen sulfide
- Hypophosphorous acid *
- **Iodine ***
- Iron fillings
- Isopropyl alcohol *
- Lead acetate
- Lithium aluminium hydride
- Lithium (batteries) *
- Magnesium sulfate
- Magnesium
- **Mercuric chloride**
- **Methamphetamine** *
- Methyl alcohol *
- **Methyl amine**
- Methyl ether ketone *
- Nitric acid
- Nitroethane
- Oxygen
- Palladium
- Palladium black
- Pentane
- Perchloric acid
- Petroleum ether
- Phenyl acetic acid
- **Phenylacetonitrile**
- **1-phenyl-2-propanone**
- 1-phenyl-2-nitropropene
- Phosgene
- Phosphine *
- Phosphoric acid *
- **Phosphorus (red) ***
- Phosphorus pentachloride
- Phosphorus oxychloride
- Platinum
- Platinum oxide
- Potassium
- Propane
- Pseudoephedrine (cold tablets)*
- Pyridine
- Raney nickel
- Sodium acetate
- Sodium bisulfite
- Sodium cyanoborohydride
- Sodium chloride *
- Sodium cyanide
- Sodium hydroxide (lye)*
- **Sodium metal ***
- Sodium thiosufate
- **Sulfuric acid (drain cleaner) ***
- Thionyl chloride
- Toluene (brake cleaner) *

The hydriodic acid/ red phosphorus method

A newer and cleaner method using ephedrine or pseudoephedrine as the main chemical precursor has gained in popularity (Irvine and Chin, 1991). The synthesis of methamphetamine from ephedrine (or pseudoephedrine) with hydrogen iodide and red phosphorus was first reported in 1981 (Frank, 1983). The first published article about methamphetamine production through ephedrine/pseudoephedrine reduction was by Skinner in "The methamphetamine synthesis via hydriodic acid/red phosphorus reduction of ephedrine" in 1990 (Skinner, 1990). This method is generally known as the Hydriodic Acid (HI) Reduction Method as shown:



The anhydrous ammonia method (Nazi method)

Ephedrine/pseudoephedrine can also be reduced to methamphetamine using the Birch method, also known as the Anhydrous Ammonia Method (or Nazi Method). Ely et. al. (1990) have described the reduction of ephedrine to methamphetamine using lithium and ammonia (Ely and McGrath, 1990). This method typically yields high quality d-methamphetamine (NDIC, 2003).

Residues at clandestine laboratories and their health risks

In a clandestine laboratory, many compounds can be present because many steps are involved in the manufacturing process. During methamphetamine production, apart from the chemicals used and products, byproducts and contaminants are also generated (Ely and McGrath, 1990; Skinner, 1990; Manning, 1999). Those compounds include flammable volatile organic compounds (VOCs), acids, bases, metals, and inorganic salts. The principal compounds which can be found in a clandestine laboratory (using HI Reduction Method or Anhydrous Ammonia Method) are the precursors, i.e. ephedrine or pseudoephedrine, alcohol, sodium hydroxide, strong acids (H_2SO_4 and HCl), solvents (such as toluene and ether) and the final product, methamphetamine. However, since chemicals can be substituted for, other chemicals can also be present. The production of methamphetamine in a clandestine laboratory is often not under ideal controlled conditions – overheating, underheating, and improper mixing can occur (Washington State Department of Health 1996). The production of methamphetamine can generate byproducts and toxic waste including phosphine gas, hydriodic acid vapour and white phosphorus (in HI Reduction Method).

This section reviews the health risks posed by clandestine laboratory residues with particular attention to the major compounds commonly found in an HI Reduction Laboratory (Tayler, 2003) as this is likely to be the dominant synthesis route owing to the ease of manufacturing together with its high yield of (+)-methamphetamine (Chan and Sulaiman et al., 2009).

Ephedrine and pseudoephedrine

Ephedrine and pseudoephedrine are precursors in the synthesis of methamphetamine in the HI reduction method (and also in Anhydrous Ammonia Method). Ephedrine is a central nervous system stimulant that may produce nervousness, anxiety, apprehension, fear, tension, agitation, restlessness, weakness, irritability, talkativeness, or insomnia (Toxnet, 2002).

High dose, acute ephedrine exposure causes severe outbreaks of sweating, enlarged pupils, spasms, and elevated body temperature, with heart failure and asphyxiation leading to death (Toxnet, 2002). The NIOSH Registry of Toxic Effects of Chemical Substances (RTECS) established LD50 (oral; rat) for ephedrine is 600 mg/kg (Washington State Department of Ecology, 2001). High dose, acute pseudoephedrine exposure causes increased blood pressure; increased, decreased or irregular heartbeat; shortness of breath, increased breathing and heart rate, mydriasis (dilated pupils), hypertension, anxiety, and vomiting (Toxnet, 2002). At the time of writing, exposure limits for ephedrine and pseudoephedrine have not been established by National Institute for Occupational Safety and Health (NIOSH), the American Conference of Governmental Industrial Hygienists (ACGIH) or Occupational Safety and Health Administration (OSHA).

Methamphetamine

Methamphetamine is the final product in the synthesis process. Previous studies have shown that it is the principal residue found at a site following a methamphetamine cook (Martyny et al, 2002). The two most common chemical forms of methamphetamine, the free base (methamphetamine base) and the hydrochloride salt (methamphetamine hydrochloride) are produced in the laboratory. Methamphetamine base is the initial product of a clandestine synthesis (Salocks and Kaley September, 2003). Because methamphetamine base is not very water soluble and is quite volatile, it is usually converted to the hydrochloride salt by bubbling hydrogen chloride gas into the methamphetamine base solution. Methamphetamine hydrochloride is usually found as yellow or white crystaline powder (Salocks and Kaley, September 2003), though other colours such as brown, grey, and pink have also been observed. Effects of methamphetamine exposure depend on a number of individual factors including age. Frequency and duration of exposure may also lead to development of tolerance (Tatsuno, Fukunaga et al., 1987) and reverse-tolerence (Tatsuno, Fukunaga et al., 1987). The estimated lethal dose is 100 mg in children and 1 g in adults . The health hazards associated with methamphetamine have been documented in a variety of sources such as in Hazardous Substances Data Bank, National Library of Medicine. Studies into the health effects of methamphetamine have included a focus on prenatal exposure during pregnancy in human and animals (Toxnet, 2002). However, as stated by Comeau (2002), none of the studies were designed to investigate the potential health effects from chronic exposure of low levels of methamphetamine (such as found in a former clandestine laboratory) to highly susceptible individuals (i.e. infants, toddlers, children and the elderly) (Comeau, 2002).

Hypophosphorous acid

Hypophosphorous acid (H_3PO_2) has been used as a substitute for red phosphorus. It can form toxic phosphine gas if overheated (NDIC, 2003; Burns, 2004) , and this poses a serious fire and explosion hazard overheated (NDIC, 2003; Burns, 2004). Hypophosphorous acid has a pH value of 0.78 (50% solution) which causes severe skin, eye, and respiratory tract irritation or burns. Hypophosphorous acid, unlike many other acids, has no smell or colour , and looks just like water, leading to the potential for accidental ingestion (Steel, 2004). At the time of writing, no exposure limits have been established for hypophosphorous acid.

Hydriodic acid

Hydriodic acid is an essential reagent in the HI reduction method. It is a corrosive acid with vapours that are irritating to skin, eyes, and the respiratory system (Burns, 2004) . It causes severe internal irritation and damage that may cause death if ingested (Burns, 2004). Hydriodic acid gas is extremely toxic and can be fatal in very small quantities (Steel, 2004). No exposure limits for hydriodic acid have been established.

Red phosphorus

Red phosphorus may be combined with elemental iodine to produce hydriodic acid. Red phosphorus in its pure form is not considered highly toxic (Salocks and Kaley, September 2003). It is non-volatile, insoluble in water, and poorly absorbed. However if red phosphorus is contaminated with white phosphorus, it may cause poisoning such as nausea, vomiting, and abdominal pain. Exposure to this contaminated red phosphorus can lead to skin, eyes, lungs, and gastrointestinal tract irritation (Salocks and Kaley, September 2003). The major hazard of red phosphorus is probably that it may explode on contact or friction. It ignites if heated above 260°C.

Iodine

Iodine crystals are combined with red phosphorus to generate hydriodic acid (HI) (Salocks and Kaley, September 2003). Iodine vapours are extremely irritating to the respiratory tract and exposure to high concentration can result in acute toxicity. Children may be more susceptible to the toxic effects of iodine vapour because they are "often less likely to leave an area where iodine vapour is present" (Salocks and Kaley, September 2003). Toxic doses of iodine can be achieved by ingestion. A dose of 2-4 g (in adults) of iodine crystals can be fatal if ingested (Salocks and Kaley, September 2003). Exposure limits for iodine have been established. The Permissible Exposure Limit (PEL) is 0.1 ppm (as a Ceiling Value). NIOSH, ACGIH, and OSHA, all have the same exposure value. The immediately Dangerous to Life and Health (IDLH) value is 2 ppm (NIOSH).

Hydrogen chloride (HCl)

Hydrogen chloride is used at the salting out stage of methamphetamine production. Cooks at clandestine laboratories often generate hydrogen chloride gas by combining sulfuric acid (e.g. drain cleaner) with sodium chloride (rock salt) (Salocks and Kaley September 2003) in a hydrogen chloride gas generator (Heinitz, 1998). It is also common to use hydrochloric acid (muriatic acid) instead of sulfuric acid (Heinitz, 1998). The container in which the reaction takes place is commonly referred to as an HCl generator (Heinitz, 1998). HCl is extremely corrosive to body tissues. HCl vapour is extremely irritating to eyes, and may cause permanent eye damage if contacted. If ingested, hydrochloric acid can cause damage to the gastrointestinal tract (Salocks and Kaley, September 2003). The Permissible Exposure Limit for HCl (PEL) is 2 ppm (as a ceiling value), while the Immediately Dangerous to Life and Health (IDLH) value is 75 mg/m^3 (50 ppm by amount) in air.

Sulfuric acid

As mentioned earlier, sulfuric acid can be reacted with salt to generate HCl gas (Heinitz, 1998). An example of common sulfuric acid is battery acid. It can also be obtained from sulfuric acid-based commercial drain cleaner. Sulfuric acid is extremely corrosive to body tissue. Inhalation causes damaging effects on the respiratory tract. It may cause blindness if it contacts the eyes. Compared to HCl, sulfuric has a lower allowable exposure level. Both OSHA PEL and NIOSH REL are 1 ppm compared to 2 ppm for HCl. The Immediately Dangerous to Life and Health Level is 15 ppm.

Sodium hydroxide

Sodium hydroxide is used in the synthesis of methamphetamine to raise the pH of methamphetamine reaction solutions. It is highly corrosive and is a powerful irritant to human body via inhalation, ingestion, and skin contact (Salocks and Kaley, September 2003). OSHA and NIOSH have the same exposure level. The Permissible Exposure Level in air is 2 mg/m^3, and the immediately dangerous to Life and Health (IDLH) is 10 mg/m^3

Solvents

There are a variety of solvents involved in methamphetamine manufacture. Acetone is a common solvent used in the manufacturing process. As acetone is volatile, its vapour irritates eyes, mucous membranes and skin. Exposure limits for acetone have been established.

Toluene is also often used as a solvent in methamphetamine manufacture, and so is commonly found in clandestine laboratories (Coxon, 2004). It is an irritant to eye, nose and throat. Exposure to toluene results in weakness, exhaustion, euphoria, dizziness and muscle fatigue (Chemwatch , 2004).

Isopropyl alcohol, ethyl alcohol (ethanol) and methyl alcohol (methanol) are irritants to eyes and respiratory (Chemwatch, 2004; Chemwatch 2004; Chemwatch 2004). Ethanol vapour can cause headaches and drowsiness (Chemwatch, 2004), while liquid ethanol can cause intoxication or even fatal if swallow in large quantity (Chemwatch, 2004). Methanol in liquid form is extremely toxic (Chemwatch, 2004), and high doses can cause death or liver and kidney damage (Chemwatch, 2004).

Phosphine gas

Phosphine is a by-product generated during the synthesis of methamphetamine using the HI Reduction method. Pure phosphine gas is colourless and odourless (Salosks and Kaley, September 2003). It is also very flammable and potentially explosive, and can ignite spontaneously on contact with air (Salosks and Kaley, September 2003). Exposure to phosphine gas can be fatal even at a very low level. The maximum limit of phosphine gas exposure without a respirator or mask is 0.3 ppm (University of Minnesota, 2000; Salosks and Kaley, September 2003). The level considered immediately dangerous to life or health is 50 ppm.

A number of cooks in clandestine methamphetamine drug laboratories have died as a result of exposure to phosphine (Russo, 1999). As most phosphine exposures occur by inhalation of the gas, children are at elevated risk if present in a clandestine laboratory because they have a greater lung surface area to body weight ratio than adults (Salosks and Kaley, September 2003). In addition, as phosphine gas is heavier than air (the vapour density of phosphine is 1.2), it may form a higher concentration at the breathing zone of children in a confined place (Salosks and Kaley, September 2003).

Other compounds

Other compounds generated from an HI reduction laboratory include flammable sludge, corrosive waste, phosphoric acid, and yellow or white phosphorus (CDPHE, 2003).

In an Anhydrous Ammonia clandestine laboratory, ammonia gas poses a great threat because it may ignite in the presence of an ignition source, and has a Lower Explosive Limit (LEL) of 15 %. When ammonia vapour dissolves in mucous fluids, it forms corrosive solutions which may cause burns to mucous membrane. Anhydrous ammonia has a PEL of 50 ppm (OSHA), NIOSH REL of 25 ppm and IDLH of 300 ppm. Lithium which acts as the catalyst in this method, is water reactive (Ely and McGrath, 1990; Salocks and Kaley, September 2003). The resulting solution is corrosive that can cause chemical and thermal burns to skin, eyes and mucous membranes (Salocks and Kaley, September 2003). Other wastes generated are flammable sludge, corrosive waste, and hydrogen chloride gas (CDPHE, 2003).

If drug manufacture methods are suspected to have included the use of mercury (typically mercuric chloride in P2P method) or lead (such as lead acetate), mercury and lead must be tested. Mercuric chloride is highly toxic, not only acutely but as a cumulative poison with an IDLH level of 10 mg/m^3 (as Hg) (2004). Lead has been known as a poisonous metal especially to nerves, and causes blood and brain disorders. It has a NIOSH REL of 0.050 mg/m^{3}and IDLH 100 mg/m^3 (as Pb) (2004).

Conclusion

The increased number of clandestine methamphetamine laboratories, whether they are at operational or non-operational stage, can lead to dangerous situations for the general public and law enforcement personnel in Malaysia. These labs can also be highly mobile, where cooks often move around to avoid detection. There is a lack of information regarding the chronic, low-level exposure to these contaminants in a residential setting, thus creating uncertainties in the establishment of “safe levels” for exposure or a cleanup standard. Regulations and guidelines for clandestine laboratory cleanup are being developed by some states within the US. Most current decontamination strategies for clandestine laboratories in the US follow the surrogate approach, and aim to ensure that the level of methamphetamine contamination is below 0.1 µg/100 cm^2. Though this standard is not health-based, it is thought to be acceptable and practical based on current knowledge and expertise. A complete guideline on clandestine laboratory residues handling and cleanup should be developed and made available especially to the law enforcement personnel in Malaysia.

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